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AND
JOURNAL OF SCIENCE.

CONDUCTED BY

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WILLIAM FRANCIS, F.L.S.

JUN 25 1917

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"Nec araneorum sane textus ideo melior quia ex secula gignunt, nec noster
vilior quia ex alienis libamus ut apes." JUST. LIPS. *Polit. lib. i. cap. 1. Not.*

VOL. XXXIII.—SIXTH SERIES.

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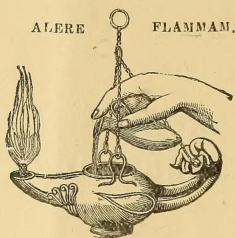
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“Meditationis est perscrutari occulta; contemplationis est admirari perspicua Admiratio generat quæstionem, quæstio investigationem, investigatio inventionem.”—*Hugo de S. Victore.*

—“Cur spirent venti, cur terra dehiscat,
Cur mare turgescat, pelago cur tantus amaror,
Cur caput obscura Phœbus ferrugine condât,
Quid toties diros cogat flagrare cometas,
Quid pariat nubes, veniant cur fulmina cœlo,
Quo micet igne Iris, superos quis conciat orbes
Tam vario motu.”

J. B. Pinelli ad Mazonium.



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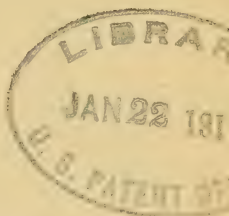
ERRATUM.

Page 373, in the numerator of the fraction on the right of equation (9)
the italic *i* should be replaced by the figure 2.

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LONDON, EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE
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[SIXTH SERIES]

JANUARY 1917.



- I. *On the Relative Behaviour of the Light Radiations emitted by Iron Vapour under the Influence of Thermal and Chemical Actions in Flames.* By G. A. HEMSALECH, *Honorary Research Fellow in the University of Manchester* *.

[Plate I.]

1. INTRODUCTION.

IN his well-known researches on air-coal gas flame spectra Dr. de Watteville has shown that by far the greater number of lines are emitted by the region of the inner blue cone and only relatively few are observed in the outer mantle †.

A few years later Dr. de Watteville and the present author established a convenient and at the same time very simple method of obtaining the spectra of flames, and were thereby enabled to extend the research to the spectra emitted by various high-temperature sources ‡. Since the method and the principal results to which it has led have not been accurately recorded in modern text-books on spectroscopy, it may be useful to state them briefly.

Our method consists in feeding the flame with the finely divided material supplied by powerful condenser discharges. The electrodes, made of the metal the spectrum of which it

* Communicated by Sir E. Rutherford, F.R.S.

† C. de Watteville, *Thèses de Doctorat*, Paris 1904; also *Philos. Trans. Roy. Soc. Series A.* vol. cciv. pp. 139-168.

‡ Hemsalech and de Watteville, *Comptes Rendus de l'Académie des Sciences*, vol. cxliv. p. 1338 (1907).

is desired to obtain, are enclosed in a glass bulb, through which is led the air or oxygen circuit feeding a coal-gas, hydrogen, or acetylene flame. The particles produced by the sparking are generally chemical compounds, mostly oxides or nitrates, and, as de Broglie has shown*, of ultra-microscopic dimensions. They therefore remain suspended in the gas for a considerable time and are carried by it into the flame, where they are vaporized.

Applying this and other methods to a study of the line-spectra of iron and calcium we obtained the following general and fundamental results † :—

1. The character of the flame-spectrum of a substance depends solely on the nature of the flame, and is not in the least influenced by the electrical or other processes used for preparing the material which is mixed with the gas.

2. In the case of solutions it is immaterial which salt of the element is used.

3. The light radiations from vapours in the outer mantles of the various flames behave as if governed by the temperatures of these flames.

4. The spectrum emitted by metal vapours in the region of the blue cone of the air-coal gas flame cannot be accounted for by simple thermal actions, but is probably due to some special chemical process prevailing in the explosion region.

In the case of iron we established the existence of two distinct groups of lines. One group, some 200 lines, is emitted by the outer mantle of the air-coal gas flame, and the lines merely increase in intensity on passing to flames of higher temperature. We considered them as the fundamental lines of the spectrum, which are easily excited by thermal actions. The other group, of over 500 lines, is emitted by the region of the blue cone only, and even in the oxy-acetylene flame we could detect only traces of some of the lines.

The object of the present research is

- a. To investigate the relative behaviour of the various types of iron lines by means of new observational and experimental methods.
- b. To gain some information with regard to the origin of the cone lines.
- c. To extend the observations to the spectra of the closely related elements cobalt and nickel.

The present paper deals only with the subject-matter mentioned under a.

* de Broglie, *Comptes Rendus*, vol. clxvi. p. 624 (1908).

† Hemsalech and de Watteville, *Comptes Rendus de l'Académie des Sciences*, vol. cxlv. p. 1266 (1907); vol. clxvi. p. 748 (1908); *ibid.* p. 859; *ibid.* p. 962; *ibid.* p. 1389; vol. cxlvii. p. 188 (1908); vol. cxlix. p. 1112 (1909); *ibid.* p. 1369; vol. cl. p. 329 (1910).

2. EXPERIMENTAL METHODS.

The feeding of the Flames.—For the air-coal gas flame the high pressure Gouy sprayer (working at from $1\frac{1}{2}$ to 2 atmospheres) and a new low-pressure electric sprayer were used; for the oxy-coal gas and oxy-hydrogen flames only the latter. The spark method described above could not be employed, for it requires a specially powerful electrical equipment. In our original experiments we made use of a Hemsalech-Tissot resonance transformer * in connexion with a Moscicki condenser of 0.05 micro-farad, working at a pressure of from 20,000–30,000 volts.

For a description of the Gouy sprayer, the reader is referred to de Watteville's original memoirs.

The Electric Sprayer.—This is an enlarged and improved form of a simple device originally intended for demonstration purposes only †. An inverted bell-jar (fig. 1) $10\frac{1}{2}$ in. high by 5 in. diameter is fitted at its narrow end with a rubber stopper, through which passes a stout wire carrying the iron electrode E_1 , and a bent glass tube G communicating by means of rubber tubing with the reservoir R. A wooden disk L, provided with a flange, forms the lid and fits air-tight on the ground edge of the jar by means of the rubber washer W. The disk is securely held by six clamps C pressing upon a steel ring F, which rests upon the flange. Through this disk pass the following glass tubes :—

1. An inlet tube A, which passes down to within an inch from the inner surface of the rubber stopper.

2. A slightly wider outlet tube B, which only just passes through the disk and is provided with a widened mouth to prevent larger drops of liquid, which collect here, from interfering with the free passage of the gas.

3. A glass tube D_1 , 6 in. high by 2 in. diameter, closed at its upper end by a cork stopper, through which passes a second tube D_2 , 12 in. long by 1 in. diameter. Into this tube is fitted the capillary D_3 passing right down the middle of the bell-jar to within about 1 in. from the electrode E_1 . Through this capillary passes a stout iron wire, the uncovered end of which forms the electrode E_2 , leaving a spark gap of $\frac{1}{4}$ in. or more between it and E_1 .

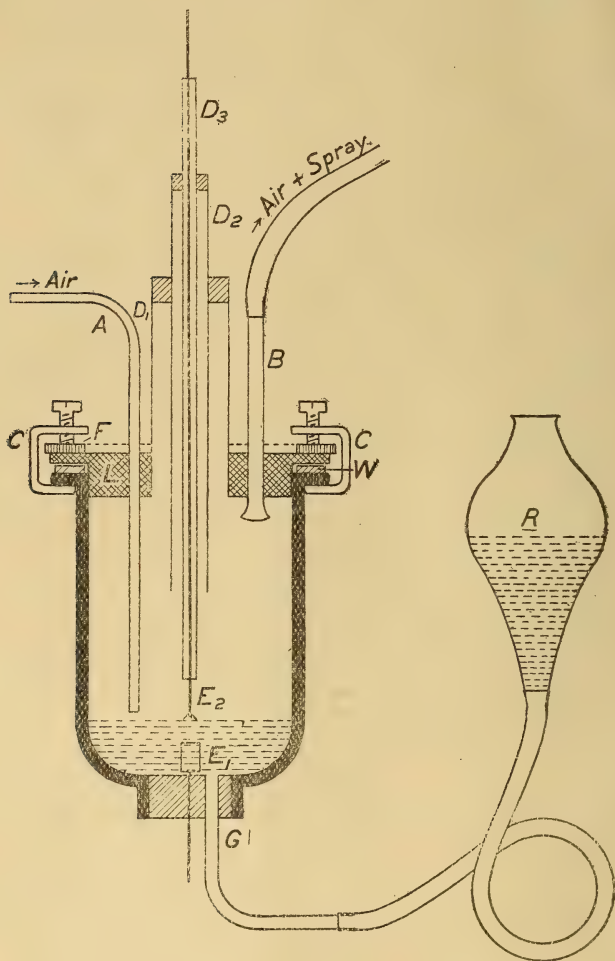
The object of these three concentric tubes is to prevent the formation of a continuous layer of conducting liquid along the inside walls of the apparatus with consequent short circuiting of the electrodes.

* Hemsalech et Tissot, *Comptes Rendus de l'Académie des Sciences*, vol. cxliv. p. 262 (1907).

† Hemsalech, Reports Brit. Assoc. Dublin, 1908.

Method of working the Electric Sprayer.—The solution of the salt to be examined, in our case a concentrated solution of perchloride of iron, is poured into the reservoir R, which

Fig. 1.



Electric sprayer.

can be fixed at any height on a clamp-stand. By means of a pinch-cock some of the liquid is allowed to flow into the sprayer until the electrode E_1 is just completely covered by it. Both electrodes E_1 and E_2 are placed in the discharge

circuit of a small plate condenser, which is connected to the secondary of an ordinary 20,000 volts transformer. An adjustable impedance coil in series with the primary prevents arcing. A shower of sparks will then pass between E_2 and the surface of the solution, and minute drops in the form of a spray are projected all round.

Air is now allowed to enter through tube A, and on its passage through the jar becomes charged with the spray. The heavier drops fall back to the bottom of the jar, but the lighter particles are carried along with the air and pass through the outlet tube B into a series of collectors, in which the material undergoes a process of refining. These collectors form an important addition both to the Gouy and the electric sprayer, for it is essential that only the very finest particles should reach the flames. I have in the main followed de Watteville's plan, both with regard to the shape and order of these collectors; his paper should therefore be consulted for details. Finally, the air carrying the spray is mixed with the coal-gas and the mixture then passed into the burner. Pressure gauges in both the air and coal-gas circuit complete the arrangement. For high temperature flames, which are fed with oxygen, the sprayer is inserted in the oxygen circuit.

Relative merits of the Gouy and electric sprayers and the Spark Method.—Although the character of the spectrum is always the same whichever method is used, the three methods do not always give equally good results, in so far as brilliancy and completeness of spectrum are concerned. Thus the spark method will not yield such well-developed spectra in the case of the air-coal gas flame as the sprayers; this I believe is due to the fact that the oxides given by the spark do not volatilize so easily at the low temperature of the air-coal gas flame. In this case, therefore, one of the sprayer methods should be employed, as it allows the use of the more volatile salts.

For the high-temperature flames the spark method is, however, to be preferred, being cleaner and more economical, and giving results so far unattained by any other method.

The electric sprayer gives good results all round, and would probably reach the standard of either of the two other methods if worked with resonance sparks.

Burners.—These form the most important item in the instrumental equipment, and special attention was paid to them from the outset. The new results obtained in this research are largely, if not entirely, attributable to the complete change of plan adopted in their construction. They

were prepared by drilling holes into plates of brass 3 mm. thick. Of the many different patterns tried only two will be described here, which have proved to be the most useful:—

Burner No. 1.—160 holes of 1 millim. diameter each, the centres of the holes being 1.5 millim. apart from each other. They are arranged in 8 rows of 20 holes each, consecutive rows being displaced in such a way that the gap between two flames of one row is opposite the flame of the next row (fig. 2). In this way a more even distribution of light is obtained. The relative position of this burner with respect to the direction of observation is indicated in the figure.

Fig. 2.

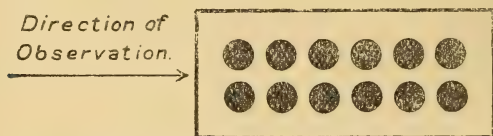


Portion of burner No. 1 enlarged 5 times.

When a low-pressure gas mixture is employed the cones obtained with this burner form an almost flat and continuous surface with only slight elevations over each hole. Seen end on the cone region presents the appearance of a bright thin line. This burner is therefore particularly suited to studying the spectrum of the explosion region.

Burner No. 2.—12 holes of 2 millim. diameter, arranged in two rows of 6 each, the distances between the centres of the holes being 3 millimetres (fig. 3).

Fig. 3.

Burner No. 2 enlarged $2\frac{1}{2}$ times.

Whenever necessary the number of holes in either burner can be reduced by closing some of them with asbestos.

There is no advantage in using more than 6 flames one behind the other, for, as Gouy has shown, a flame charged with radiating vapour absorbs about 50 per cent. of a similar flame placed behind it.

The gases in the air-coal gas mixture were so proportioned as to produce blue-coloured cones; it was found that the light emission by the metal vapour was at a maximum in this case. The heights of the cones given by burner No. 2 were from 3 to 8 millimetres, according to the velocity of the gas mixture.

Burners for oxy-coal gas and oxy-hydrogen flames.

The burner selected was one in which the two gases are mixed before being burnt. The oxygen and coal-gas or hydrogen arrive through separate channels at the base of a small mixing-chamber, and thence pass through a short tube, about 2 in. long, to the nozzle from which the mixture escapes through an orifice of 1 millim. diameter.

Burner for oxy-acetylene flame.

This was one of the ordinary industrial type and not really suitable for spectroscopic work, but no other pattern was available at the time. The acetylene passes into the mixing-chamber at low pressure. The oxygen, on the other hand, is forced under pressure through a very fine orifice into the mixing-chamber and diffuses into the acetylene. The mixture then passes through the nozzle and a 1 millim. orifice. It was, of course, impossible to charge the oxygen with the material from a sprayer, because the fine orifice through which the oxygen has to pass becomes immediately clogged. So the spray from a Gouy apparatus was passed into the outer parts of the flame by means of a jacket fixed round the nozzle of the burner. This is a bad method of obtaining the spectrum of a flame, for the material does not pass through the cone region and I adopted it, though most reluctantly, only because previous experience with the oxy-acetylene flame had shown me that iron vapour does not emit spectrum radiations in the inner cone of this flame. In the case of nickel and cobalt this method failed altogether.

Spectrograph and projection apparatus.

A serviceable spectrograph was constructed out of the remains of a Kirchhoff and Bunsen four-prism spectroscope*. Only three prisms were available, each having a refracting angle of 45° . The objective of the observing telescope was

* The original instrument is described in Roscoe-Schuster's 'Spectrum Analysis,' p. 70 (1890).

mounted at the end of a long box-camera, and the collimator provided with a platino-iridium slit, made by Adam Hilger. All these parts were then mounted and securely fixed in a strong teak-wood case. The instrument was used in a vertical position, with the slit horizontal.

Special attention was paid to the projection lenses, for it was essential that the image of the source of light formed on the slit should be as perfect as possible. A Zeiss objective of 25 cm. focal length was used for projecting an image of the flame, and a Dallmeyer portrait objective for the comparison spark. All the various methods and manipulations used in adjusting and focussing the spectrograph and in the centreing and waxing down of all the optical parts, including the projection objectives, have been fully described in my thesis*.

Since the low-pressure air-coal gas flame burns vertically upwards, its image on the slit is in a direction at right angles to the latter. Sometimes, however, it became necessary to form the image parallel to the slit. This was done by means of a system of two silver-on-glass mirrors, which were placed immediately behind the Zeiss objective and rotated the beam of light through 90° . These mirrors were silvered by Martin's process and coated with a very thin film of celluloid in order to prevent tarnishing by the fumes from the flame.

Support for burners.

It was necessary, especially when observing the explosion region with burner No. 1, to adjust the image on the slit with some degree of accuracy; for this reason the burners were mounted on a support with vertical motion. This support was provided by the unemployed telescope tube of the above-mentioned spectroscope, the focussing tube serving as holder for the burners, the rack-and-pinion movement constituting an excellent fine adjustment.

Self-induction spark † for comparison spectrum.

The electrodes, in the shape of rounded-off cones or cylinders, are fixed in a horizontal position, with a gap of about 5 millim. between them: the sparks thus pass in a direction parallel to the slit. They are produced by a small plate condenser of 0.01 micro-farad capacity contained in a lead-lined box filled with paraffin-oil. In one branch of the

* Hemsalech, *Thèses de Doctorat*, pp. 33-41 & p. 55 (Paris, 1901).

† Hemsalech, *Comptes Rendus de l'Académie des Sciences*, vol. cxliv, p. 692 (1907).

discharge circuit, and in series with the spark gap, is a self-induction coil of 0.05 henry. The condenser receives its charge from the secondary of a 10-in. Apps coil, the primary of which is fed with pulses of continuous current at the rate of about 5 per second through the medium of a Rochefort plunger break, working in an atmosphere of coal-gas.

Reduction of spectrograms.

The plates were measured on a Perreaux dividing engine* which had been fitted with a travelling platform for the purpose. Since it was merely a question of identifying known lines, the wave-lengths were derived by linear interpolation. The plan adopted was similar to that laid down in my thesis (page 56).

Relative intensities of lines.

These, of course, refer to the photographic intensities, and are estimated on quite an arbitrary scale. Feeble lines are marked $\frac{1}{2}$, very feeble ones 0 and 00. Lines of moderate strength 1, 2, 3, and 4; strong lines 6, 8, and 10; extra intense 12 and 15.

3. GENERAL CHARACTER OF THE SPECTRUM EMITTED BY IRON VAPOUR IN THE AIR-COAL GAS FLAME.

Difference between cone and flame lines.

De Watteville's observations had brought out the interesting fact, already mentioned, that the majority of lines are emitted by the region of the blue cone, so that, when an image of the flame is formed on the slit parallel to the latter, the cone lines are seen to reach only as far up as the bands of the Swan spectrum. The flame lines, on the other hand, pass beyond the boundary of the cone region into the flame above. The flame lines are alone observed when the substance to be examined is introduced into the flame by any of the older methods—for example, by means of a platinum wire.

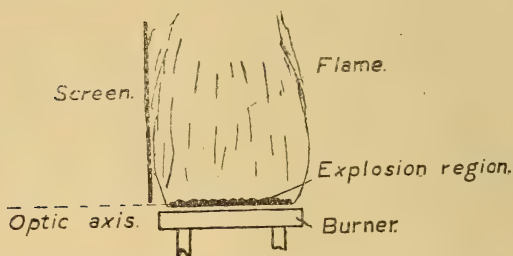
Flame lines emitted by cone.

Since the cone of an ordinary flame is always and everywhere surrounded by a layer of flame, we always see the flame lines superimposed upon the cone lines, and it is impossible in these circumstances to decide whether flame lines are likewise excited in the cone or whether the latter emits solely its characteristic lines. In order to settle this

* A description of the instrument is given in Stewart and Gee's 'Practical Physics,' vol. i. p. 16 (1885).

point a series of experiments were made, of which one may be mentioned here. A flat explosion surface was obtained by means of burner No. 1 and placed in the optic axis of the collimator (fig. 4). A metal screen was fixed in front of

Fig. 4.



Method of observing spectrum of explosion region.

the flame in such a way that only light from the explosion region could pass along the axis. It is true that a thin stratum of flame remained at the end of the explosion surface, but it was small compared with the depth of the latter, and, if no flame lines were emitted by the explosion region, their intensities should appear appreciably reduced relative to the cone lines. But the resulting photographs show no indication whatever of a relative weakening of the flame lines.

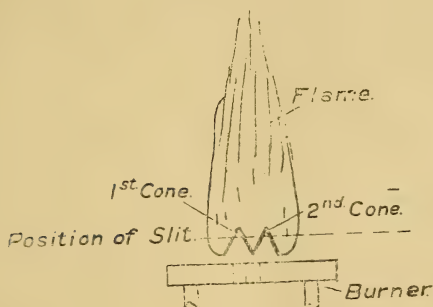
Similar results were obtained with other burners by examining the explosion region near the base of the cones. We must therefore conclude that the emission of flame lines is already initiated during the passage of the material through the thin film of the explosion region. This was further corroborated by some of my later photographs, which show a slight intensification of these lines in the cone region.

Cone lines emitted by flame.

The superior definition of the image of the flame on the slit due to the new type of burner used, and also to the excellent correction of the Zeiss projection-objective, has brought out an interesting and important new fact, which had not been observed in our previous experiments—namely, that many of the lines formerly included in our class of fundamental lines occupy in reality a position intermediate between these and the lines of the supplementary spectrum. They are cone lines in the sense that they are strongly emitted by the cone, but only feebly emitted by the flame.

*Explanation of Plate I, figs. 1 & 2 (enlarged 5 times).—*The spectrograms were obtained by means of burner No. 2. The appearance of the flame and cones, as seen in the direction of the collimator axis, is shown in fig. 5. The two cones are

Fig 5.



Method of observing spectrum of air-coal gas flame with burner No. 2.

completely enveloped by the flame. An image was formed on the slit in such a way that the latter passed across the cones at a point situated about two-thirds up from the base. It will be seen that with this arrangement the resulting photograph shows two spectra due to the cones, which are, as it were, imbedded in the spectrum of the flame. On the two cone spectra there are superimposed spectra, due to those parts of the flame, situated immediately in front and behind the cones. This is, of course, unavoidable, but must be borne in mind when interpreting the photograph.

The spectrograms obtained in this way show in a most striking manner the relative sensitiveness of the various vibrations to the chemical and thermal forces which prevail in the cone and flame respectively.

The flame lines appear as long lines passing right through the spectra of the cones and beyond—for example, the lines 3860, 3920, and 4376. It will be noticed that over the cone spectra they seem slightly enhanced. This may be due either to a real enhancement by chemical action, or to the superposition of the two emissions from the cone and the portions of the flame in front and behind, as already referred to.

The most remarkable feature of those cone lines which

are likewise emitted by the flame is the abruptness in the decrease of intensity on passing from the region of chemical to that of thermal actions, as is so well illustrated by the triplets at 4046 and 4384.

As the most prominent example of the lines of our supplementary spectrum, may be cited the group at 4957. These lines show absolutely no trace in the flame.

Relative behaviour of flame and cone lines in high-temperature flames.

As M. de Watteville and myself have shown, all the flame lines increase in intensity on passing to the oxy-coal gas, oxy-hydrogen, and oxy-acetylene flames, whereas the lines of the supplementary spectrum appear only as traces in the last-named flame. Those of the cone lines which show feebly in the mantle of the air-coal gas flame are likewise enhanced in the high-temperature flames.

The sensitiveness to temperature changes is, however, not the same for all the lines, some lines being more enhanced than others. Thus the lines 3720, 3737, and 3746, which are relatively feeble in the air-coal gas flame, appear relatively bright in the oxy-acetylene flame. The characteristic features of a high-temperature flame-spectrum are shown in the reproduction of a portion of the oxy-acetylene spectrum on Plate I. fig. 3 (no. 1) which should be compared with the air-coal gas flame and cone spectra on Plate I. fig. 1.

Comparison of flame-spectrum with that of self-induction spark.

On Plate I. fig 3 (no. 2), the spectrum of the self-induction spark is placed in juxtaposition with that of the oxy-acetylene flame. It will be seen that the flame lines, which are so intense in No. 1, are relatively feeble in No. 2; examples are the lines at 3720, 3860, and 3920. On the other hand, the cone lines which are relatively feeble in No. 1, such as 3816 and 4046, are relatively strong in the spark. As M. de Watteville had already observed, the spectrum given by the self-induction spark, indeed, approaches that of the air-coal gas cone. There are, however, certain lines which are enhanced in the self-induction spark, and these may be assumed to be specially sensitive to electric actions.

It thus seems that the chemical actions, to which the iron vapour is subjected in the explosion region of the air-coal

gas flame, has an almost as far-reaching effect on the atomic systems concerned as the electric actions in the spark-discharge.

4. CLASSIFICATION ON LINES BASED ON THEIR RELATIVE BEHAVIOUR IN FLAMES.

The results of all the measurements and observations were tabulated so as to show at a glance the relative intensity and character of each line in the various sources of light examined. With the help of this table the lines were classed according to their behaviour in the various flames, and the following classification was provisionally adopted:—

Class I. Lines which are emitted by the mantle of the air-coal gas flame, and gain in intensity on passing to the high-temperature flames. They are specially sensitive to thermal actions, and may be regarded as true temperature lines.

Class II. Lines which are particularly sensitive to the special chemical actions of which the explosion region of the air-coal gas flame is the seat. They are also, though feebly, emitted by the outer mantle. In the flames of higher temperatures their intensities increase, showing that they likewise respond to thermal changes, but to a lesser degree than Class I. lines.

Class III. This class contains the bulk of the cone lines which form what M. de Watteville and myself had called the > supplementary spectrum.

The following lists contain lines of Classes I. and II. only. Those of Class III., for the same region of the spectrum, can easily be obtained from de Watteville's table by eliminating the lines given here. The lines near the extremities of the spectrum appear all relatively feeble. This is due to the absorption of the glass in the ultra-violet, and to the low sensitiveness of the photographic plates employed to the green part of the spectrum. Wave-lengths are expressed in international units. Lines to which an asterisk is affixed are marked on Plate I. figs. 1, 2, & 3 to the nearest unit.

CLASS I.

Lines sensitive to thermal actions.

| λ . | Relative Intensity. | λ . | Relative Intensity. | λ . | Relative Intensity. |
|-------------|---------------------|-------------|---------------------|-------------|---------------------|
| 3570·12 | 00 | *3737·13 | 8 | 3927·94 | 8 |
| 3581·20 | 00 | *3745·55 | 10 | 3930·30 | 10 |
| 3608·85 | 00 | *3745·91 | | 4216·18 | 2 |
| 3618·77 | 00 | 3748·25 | 4 | *4375·93 | 4 |
| 3631·46 | 0 | 3824·44 | 8 | *4427·31 | 3 |
| 3647·84 | 0 | *3856·38 | 8 | *4461·65 | 3 |
| *3679·92 | 2 | *3859·90 | 12 | *4461·99 | |
| 3687·45 | 00 | 3878·67 | 10 | *4482·27 | 1 |
| *3705·56 | 3 | 3878·73 | | 4489·74 | 0 |
| 3707·91 | 00 | *3886·29 | 15 | 4490·08 | |
| 3709·24 | 0 | 3895·65 | 6 | 5012·07 | 0 |
| *3719·93 | 10 | *3899·70 | 8 | 5167·49 | 0 |
| 3722·57 | 4 | 3906·47 | 4 | 5269·53 | 1 |
| 3727·63 | 0 | *3920·26 | 6 | 5328·06 | 00 |
| 3733·32 | 3 | 3922·92 | 8 | 5371·50 | 00 |

CLASS II.

Lines sensitive to chemical actions.

| λ . | Relative Intensity. | λ . | Relative Intensity. | λ . | Relative Intensity. |
|-------------|---------------------|-------------|---------------------|-------------|---------------------|
| 3558·52 | 00 | 3834·23 | 4 | 4177·60 | 0 |
| 3565·38 | 00 | 3840·44 | 2 | 4202·04 | 5 |
| 3584·65 | 00 | 3849·99 | 2 | 4207·13 | $\frac{1}{2}$ |
| 3586·97 | 00 | 3865·53 | 2 | 4227·44 | 4 |
| *3734·86 | 6 | 3872·51 | 3 | 4250·13 | 3 |
| 3743·37 | $\frac{1}{2}$ | 3878·02 | 2 | 4250·79 | |
| 3749·47 | 5 | 3888·52 | 4 | 4260·48 | 5 |
| 3758·23 | 3 | 3897·88 | 1 | 4271·16 | 3 |
| 3763·80 | $2\frac{1}{2}$ | 3902·95 | 5 | 4271·75 | |
| 3767·19 | 2 | 3917·17 | 00 | 4294·13 | 1 |
| 3787·88 | 1 | 3969·26 | 6 | 4307·92 | 10 |
| 3795·00 | 2 | 4005·26 | 5 | 4325·78 | 10 |
| 3798·50 | $\frac{1}{2}$ | *4045·82 | 12 | *4383·55 | 15 |
| 3799·55 | 1 | 4063·61 | 10 | 4404·75 | 8 |
| 3812·88 | 1 | 4071·75 | 10 | 4415·13 | 4 |
| *3815·84 | 6 | 4132·08 | 6 | 4528·62 | 1 |
| 3820·44 | 8 | 4132·90 | | | |
| 3825·90 | 6 | 4143·43 | 8 | | |
| | | 4143·88 | | | |

5. STRUCTURE OF IRON SPECTRUM.

After a simplification of the spectrum had been achieved, as explained in this paper, and lines of common origin classed together, it was, of course, natural to look for the possible existence of still closer relationships connecting lines or groups of lines of the same class. Although no

evidence for the existence of series, such as are known in the case of a number of other elements, has so far been detected, it is impossible to pass over without comment the curious groups of lines which have been encountered in various parts of the spectrum. These groups consist of three, four, or more lines, the characters and relative positions of which are such as to suggest some orderly arrangement.

In order to facilitate the search for these groups, a series of normal spectra were drawn, each spectrum containing lines of only one class. To the three classes given by the flames was added that for the self-induction spark from which all the flame lines had been eliminated.

The principal groups obtained in this way are given hereafter. Δ_1 , Δ_2 , &c., signify first, second, &c., differences. The symbol $d?$ means that the line is a double one in the arc, but that it was not resolved by my spectrograph. It was, therefore, not possible to ascertain which of the two components belongs to the group, and an error may have been made in the selection of the line. An asterisk added to the wave-length number indicates, as before, that the line is marked to the nearest Ångström unit on the accompanying plates.

Class I. Groups.

| Wave-lengths. | Oscillation Frequency. | Δ_1 . | Δ_2 . | Δ_3 . |
|---|--|-------------------------|----------------|--------------|
| $\alpha.$ { *3679.92 *3705.56 3722.57 3733.32 | 27174.5 26986.5 26863.2 26785.8 | 188.0 123.3 77.4 | 64.7 45.9 | 18.8] |
| $\gamma.$ { *4375.93 *4427.31 *4461.65 $d?$ *4482.27 | 22852.3 22587.1 22413.2 22310.1 | 265.2 173.9 103.1 | 91.3 70.8 | 20.5 |
| $\delta.$ { 5012.07 5167.49 5269.53 5328.06 | 19951.8 19351.7 18977.0 18768.6 | 600.1 374.7 208.4 | 225.4 166.3 | 59.1 |
| $\beta.$ { *3856.38 3878.73 $d?$ 3895.65 3906.47 | 25931.0 25781.6 25669.7 25598.6 | 149.4 111.9 71.1 | 37.5 40.8 | |
| { *3719.93 *3737.13 *3745.55 $d?$ | 26882.2 26758.5 26698.4 | 123.7 60.1 | | |
| { *3859.90 *3886.29 *3899.70 | 25900.7 25731.5 25643.0 | 169.2 88.5 | | |

Of the quartet groups, α , γ , and δ are the most interesting. It will be noticed that the distances between their components grow less on passing to groups of shorter wave-lengths, the variations, as indicated by the Δ 's, being approximately as $1 : \frac{1}{2} : \frac{1}{3}$. Group β may possibly be connected with the quartet group 4903 of the self-induction spark (see below). In regard to the two triplets, it may be mentioned that the distances between their components are approximately as $2 : 1$.

Class II. Groups.

| Wave-length. | Oscillation Frequency. | Δ_1 . | Δ_2 . |
|---------------|------------------------|--------------|--------------|
| *3734.86 $d?$ | 26774.8 | 104.4 | 42.3 |
| 3749.47 | 26670.4 | 62.1 | 22.7 |
| 3758.23 | 26608.3 | 39.4 | 15.5 |
| 3763.80 | 26568.9 | 23.9 | |
| 3767.19 | 26545.0 | | |
| 4271.75 $d?$ | 23409.6 | 196.5 | |
| 4307.92 | 23213.1 | 95.9 | |
| 4325.78 | 23117.2 | | |

In addition to the triplet here given, three more were found in this class, among which were the two well-known triplets at 4046 and 4384. Also here the ratio between the frequency differences of successive components is approximately as $2 : 1$. The quintet at 3735 stands out most prominently in the spectrum of the air-coal gas cone, but in the oxy-acetylene flame it is quite insignificant as compared with the brilliancy of the temperature lines in its neighbourhood (compare Plate I. figs. 1 & 3).

In all the groups of Classes I. and II. the head line is on the most refrangible side, the groups converging towards the red.

Class III. Groups.

| Wave-length. | Oscillation Frequency. | Δ_1 . | Δ_2 . | Δ_3 . | Δ_4 . |
|---------------|------------------------|--------------|--------------|--------------|--------------|
| 4466.56 | 22388.6 | 47.4 | | | |
| 4476.03 | 22341.2 | 92.1 | 44.7 | 42.9 | |
| 4494.57 | 22249.1 | 179.7 | 87.6 | 76.9 | 34.0 |
| 4531.16 | 22069.4 | 344.2 | 164.5 | 105.2 | 28.3 |
| 4602.95 | 21725.2 | 613.0 | 269.7 | | |
| 4736.79 | 21111.3 | | | | |
| 4859.76 | 20576.5 | 48.2 | | | |
| 4871.33 $d?$ | 20528.3 | 81.7 | 33.5 | 2.1 | |
| 4890.78 $d?$ | 20446.6 | 117.3 | 35.6 | 4.2 | |
| 4919.01 $d?$ | 20329.3 | 157.1 | 39.8 | | |
| *4957.31 $d?$ | 20172.2 | | | | |

The distinguishing feature of the groups in this class is that they, unlike the groups in Classes I. and II., converge towards the ultra-violet. In regard to the first group, it is possible that it continues beyond 4737, but my observations in this part of the spectrum have been greatly impeded by the presence of a strong continuous spectrum, which, combined with the low dispersion of my spectrograph, would naturally obliterate all but the strongest lines. To try and bring in further lines by extrapolation is almost hopeless, in view of the fact that the wave-lengths are possibly uncertain to within 0.05 of a unit, and, further, the number of remaining spark or arc lines in that region is so great that coincidences could always be found.

The last four lines of the second group are close doublets both in arc and spark. But on a photograph taken of this region by M. de Wetteville and myself with a high dispersion, I noticed that in the air-coal gas cone only one of the components is brought out. As I have now not access to this document, I am not sure that it is the more refrangible component.

In addition to the above two groups, there is a quartet with the head line at 4022.

Groups in the spectrum of self-induction spark.

| Wave-length. | Oscillation Frequency. | Δ_1 . | Δ_2 . |
|---|---|---|---|
| $\left\{ \begin{array}{l} 4903.32 \\ 4938.83 \\ 4966.10 \\ 4985.26 \text{ } d? \end{array} \right.$ | $\left\{ \begin{array}{l} 20394.3 \\ 20247.7 \\ 20136.5 \\ 20059.1 \end{array} \right.$ | $\left\{ \begin{array}{l} 146.6 \\ 111.2 \\ 77.4 \end{array} \right.$ | $\left\{ \begin{array}{l} 35.4 \\ 33.8 \end{array} \right.$ |

The frequency differences between the components of the above group are nearly the same as those for group β of Class I., and it is not unlikely that there is some relation between the two.

In addition to this group, there is another quartet with head line at 5400, likewise converging towards the red.

It is quite possible that these two groups are really constituted of temperature lines and belong to Class I.

Although all the flame lines had been eliminated from the spectrum of the spark, it seems probable that the remaining spectrum is still a mixture of lines of different character. For this reason no special attention has been devoted to this class for the moment.

6. CONCLUDING REMARKS.

In surveying the results so far obtained, it must be borne in mind that the present research is necessarily only of a preliminary nature, owing to the restrictions imposed by the optical means employed. Nevertheless, most valuable information and experience have been gained, which will prove of great help in planning the course along which future research will have to be conducted. Thus the division of lines into classes might profitably be carried still further by taking into account the various types of enhanced lines, to which I drew attention at the last meeting of the International Union for Solar Research *. This, combined with an extension of the spectral region examined in the ultra-violet and towards the longer wave-lengths, would, no doubt, bring in many more line groups, and perhaps ultimately lead to the discovery of the complete structure of the spectrum. The grouping of apparently connected lines which has, so far, been accomplished as a result of this investigation, may be regarded as a first step in that direction.

In conclusion, I desire to express my gratitude to Sir Ernest Rutherford for the most generous hospitality which he is extending to me in his laboratory, and to thank him for the kind interest he is taking in the work.

My thanks are also due to Professor Beattie, in whose laboratory workshop many of the apparatus used in this research have been constructed.

Manchester, Nov. 2, 1916.

II. *Visual Diffusivity.* By HERBERT E. IVES †.

1. Introduction.
2. Application of the Idea of Diffusivity to Instantaneous Light Sources.
3. Qualitative Observations on Retarded Images and After-Images.
4. Measurements.
5. Discussion.

1. *Introduction.*

IN two previous papers by the writer and Mr. E. F. Kingsbury ‡ on "The Theory of the Flicker Photometer," the idea has been developed that the transmission of impressions from the retina to the brain is in accordance

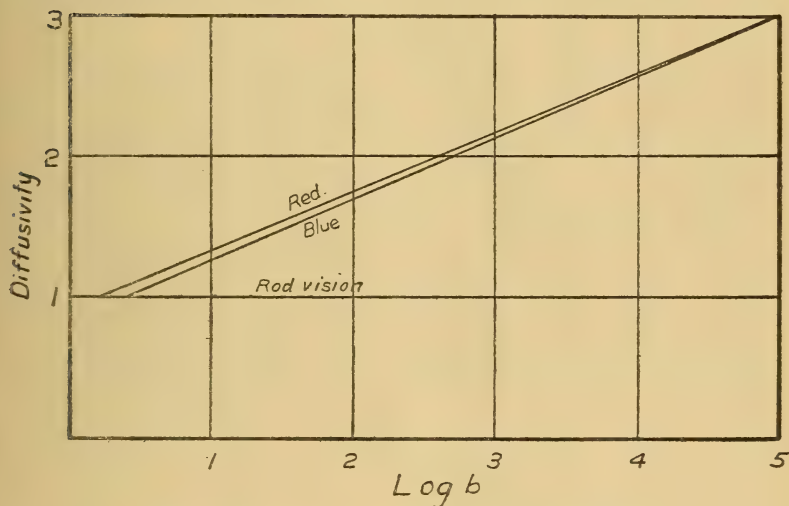
* Bonn, 1913.

† Communicated by the Author.

‡ Ives and Kingsbury: "The Theory of the Flicker Photometer."—
I. & II. Phil. Mag., Nov. 1914, p. 708; April 1916, p. 290.

with the physical laws of conduction. The chief experimentally established phenomena of the flicker photometer find explanation in the assumption that the stimulus is transmitted through a layer of matter having a coefficient of *diffusivity* which is different for different colours and varies with the intensity of the stimulus. In accordance with our previous work, the diffusivity for coloured light is a rectilinear function of the logarithm of the stimulus intensity. For colourless or rod vision the diffusivity is constant. These relations are exhibited diagrammatically in fig. 1.

Fig. 1.



Diagrammatic representation of brightness-diffusivity relation for red, blue, and rod vision.

This conception of the visual process has not only served to explain previously known facts in the realm of intermittent vision, but has indicated others not heretofore observed. The phenomena of flicker are, however, of such a complex character that, satisfactory as this hypothesis has been, it may have appeared to some to be insufficiently supported so long as it played no part in explaining other simpler phenomena.

The present paper deals with the visual parallel to one of the simplest cases of heat conduction, in which the diffusivity of the conducting layer figures, namely that of *instantaneous*

heat sources. This, in the case of light, is of course the case of single brief exposures. It is shown below that, in accordance with our theory, a difference of diffusivity should result in a difference in the time of perception after exposure. This predicted difference has been found both in the case of light of one colour but different intensity and in the case of lights of different colour and the same intensity. In addition, the positive after-image has been indicated to be simply the rod-vision impression delayed in transmission by the low diffusivity peculiar to this kind of vision. Both the new phenomena of differential rate of transmission for photopic stimuli and the relation of the colourless after-image to the photopic images have been subjected to quantitative measurement with results supporting the theory.

2. *Application of the Idea of Diffusivity to Instantaneous Light Sources.*

It is shown in treatises on heat conduction that the temperature V of a conducting slab of diffusivity K , at a depth X , at a time t after the instantaneous application to the surface of a quantity of heat Q is

$$\frac{Q}{2\sqrt{K\pi t}} e^{-\frac{X^2}{4Kt}} \dots \dots \dots (1)$$

Now the time at which this is a maximum may be found by differentiating (1) with respect to t . This gives

$$t_m = \frac{X^2}{2K}, \dots \dots \dots (2)$$

or the interval between reception and perception of a stimulus is inversely as the diffusivity.

The measurement of this interval is obviously not feasible, but the *difference* between the intervals for two stimuli is measurable. Several special cases may be treated:—

1st Case.

One colour, two intensities, I_1 and I_2 ; $I_2 > I_1$.

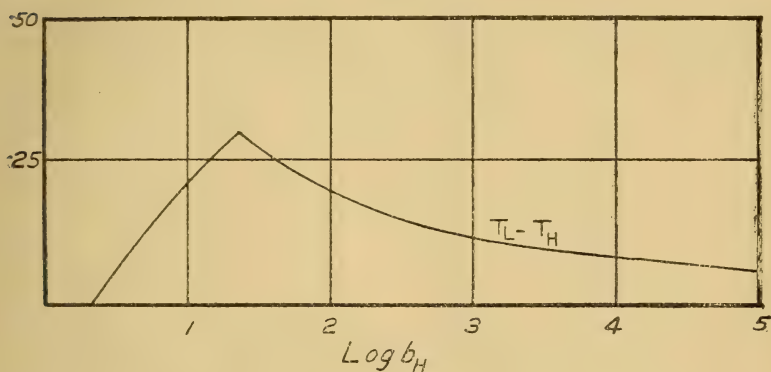
$$t_1 = \frac{1}{a \log I_1 + b}, \dots \dots \dots (3)$$

$$t_2 = \frac{1}{a \log I_2 + b}, \dots \dots \dots (4)$$

$$t_1 - t_2 = \frac{1}{a \log I_1 + b} - \frac{1}{a \log I_2 + b} \dots \dots \dots (5)$$

This case is plotted in fig. 2, using the data of fig. 1, taking $I_2 = 10 I_1$. The less intense image should be seen later than the more intense by an interval which should increase with decreasing intensity. If the observation is by

Fig. 2.



Time-interval between a high intensity and a low intensity image (differing ten times in brightness), as calculated from the data of fig. 1.

blue light, which goes over into rod vision at the lowest intensities, this interval again decreases, becoming zero when the diffusivity is constant and the same for both images. This is the case represented.

2nd Case.

Two colours, red and blue, of the same intensity.

$$t_R = \frac{1}{a \log I + b}, \quad \cdot \cdot \cdot \cdot \cdot \cdot (6)$$

$a < c; \quad b < d,$

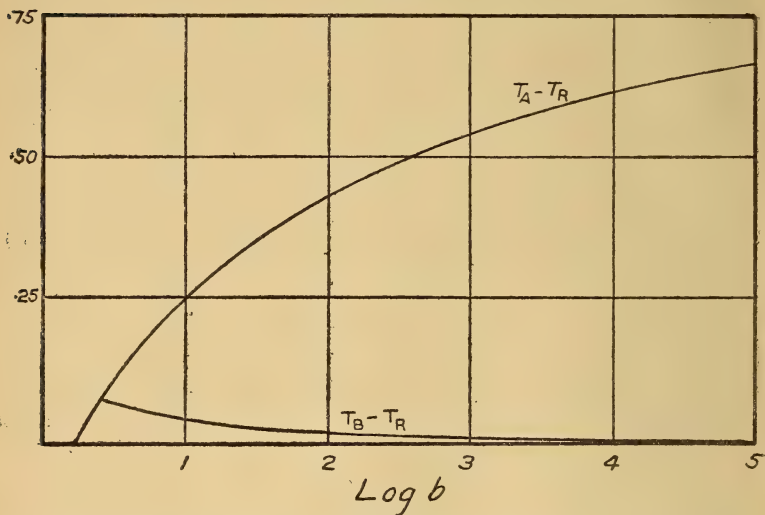
$$t_B = \frac{1}{c \log I + d}, \quad \cdot \cdot \cdot \cdot \cdot \cdot (7)$$

$$t_B - t_R = \frac{1}{c \log I + d} - \frac{1}{a \log I + b} \cdot \cdot \cdot \cdot (8)$$

This case is plotted in fig. 3, again using the data of fig. 1. For all intensities shown on the plot the blue image will be seen later than the red. At high intensities the interval will be smaller than at low. At very low intensities, where the

blue image merges into the rod image the red and blue will again approach each other.

Fig. 3.



Time-interval between blue and red, and between red and after-images, calculated from data of fig. 1.

3rd Case.

A coloured (photopic) image, and a colourless (scotopic) image.

It has been a debated question whether the colourless rod image is actually present at high intensities. On the assumption that it is, we have the condition

$$t_C = \frac{1}{a \log I + b}, \quad \dots \dots \dots (9)$$

$$g < a \log I + b,$$

$$t_A = \frac{1}{g}, \quad \dots \dots \dots (10)$$

$$t_A - t_C = \frac{1}{g} - \frac{1}{a \log I + b} \quad \dots \dots \dots (11)$$

If we call the rod image the after-image, it should lag behind the photopic image by an interval which increases with the intensity in the manner shown in fig. 3. If the interval is measured after a blue image it becomes zero

where this image merges with the rod image. If measured after a red image it becomes equal to the blue-red interval at the same point.

3. Qualitative Observations on Retarded Images and After-Images.

(a) Apparatus.

The apparatus, which was designed so as to permit of measurement of the time-interval between two impressions, is shown diagrammatically in fig. 4. It consists essentially

Fig. 4.

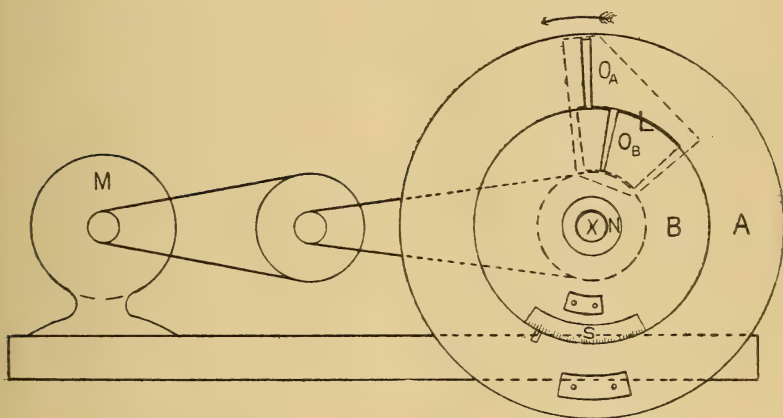


Diagram of apparatus for studying interval between perception of images of different brightness and colour.

of two superposed circular disks of sheet metal, A and B, one 22 cm. the other 36 cm. diameter, both mounted on the same axis, X, and locked in any relative angular relation by the nut N. In each disk is narrow radial slot, O, of five degrees opening, the relative positions of these slots being variable from coincidence of direction up to about sixty degrees divergence, as read on the scale S. On the back of the larger disk is mounted a piece of flashed opal glass which is illuminated by the light source behind and is the actual bright surface observed. Grooved holders are provided over O_A and O_B for carrying coloured or other glasses, and the small streak of light between the disks at L is covered by strips of electric wiring tape. The disks are rotated slowly by an electric motor with a multiple reduction pulley system by which speeds of one revolution per second and less are

obtainable. Speeds are measured by an electric tachometer. An elaborate screening system is provided so that no light gets around the edge of the disks, and observations are made at one metre distance in a darkened chamber.

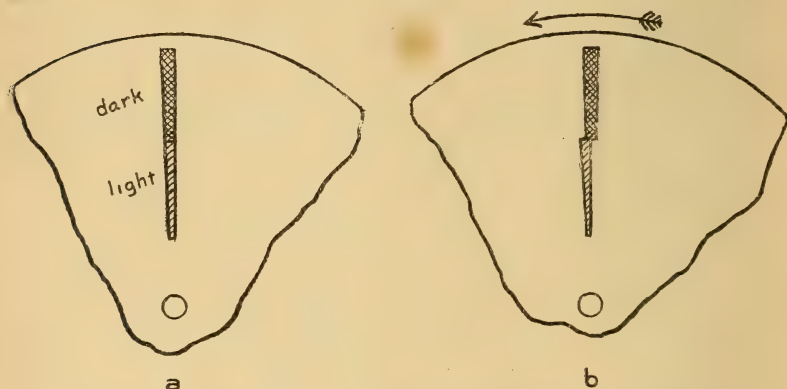
The principle which the apparatus is planned to utilize is a familiar one. If the slot O_A be imagined covered with a glass to reduce its intensity, or with a coloured glass of a hue more towards the blue than that of O_B , the theory just developed predicts that on rotating the disks in the counter-clockwise direction, with the slots exactly in line, they will be seen not in line, but the slot O_A will appear to lag behind or be displaced. If this occurs, then it will be possible to move the disk B in the clockwise direction until on rotation the two slots again appear in line. Knowing the angle by which the slots have been turned with respect to each other, and the angular velocity of the disks, it is easy to calculate the interval of time by which one impression is delayed behind the other.

Before attempting quantitative measurement of these phenomena they were studied in detail qualitatively, and a description of these observations follows:—

(b) *Light and dark stimuli of the same colour.*

The slot O_A is covered by a neutral tint glass, the two slots being in line, and the disks are slowly rotated. At a fairly low intensity of illumination (illumination and other

Fig. 5.



Appearance of adjacent dark and light apertures, or blue and red apertures: *a*, stationary; *b*, in motion.

constants are given in the description of the measurements) the dark slot appears several degrees behind the other, presenting the appearance shown in fig. 5*b*. At high

intensities this phenomenon is less marked, as it is again at very low ones. *The prediction of theory is confirmed.*

(c) *Red and blue light.*

The slot O_A is covered by a good blue glass, which transmits no red, and the slot O_B by a red signal glass. On rotation the blue image lags behind by several degrees, presenting the appearance already depicted by fig. 5*b*, substituting the difference of colour for the difference of intensity which the figure indicated when referring to the last section.

This lagging of one colour behind the other is a very striking phenomenon, well suited to demonstration to a small audience. The effect is most extraordinary if the disk, instead of being rotated, is rapidly oscillated through five or ten degrees, when the blue image may be made to vibrate entirely out of phase with the red, appearing as though attached to it by a cord. It is not an effect that has to be glimpsed after painful preparation by a trained eye, but an optical delusion of most convincing verisimilitude. On its being exhibited without comment to the mechanic who made the apparatus, he immediately assumed that he had been called in to correct a mechanical slip between the disks!

At the very high intensity obtained by placing a carbon arc lamp about 35 centimetres behind the flashed opal glass of the disk, the lag of blue behind red is practically absent; it was not found possible with the intensities at our disposal to demonstrate a reversal of the red and blue positions, such as theory indicates for some excessively high intensity, beyond the crossing point of the red and blue diffusivity lines of fig. 1.

(d) *Purple light.*

If the various colour impressions are transmitted by entirely independent channels, it would follow that a narrow line of a mixed colour such as purple ought to be resolved into its constituents when passed across the field of vision. Dr. Karrer informs me that he has observed a moving bright light spread out into a spectrum in a way which would meet with explanation in this way. I was not able, however, to obtain a clear cut and unmistakable resolution of any purple I tried with this apparatus. This agrees with the conclusion drawn from the previous work with the flicker photometer with unequal exposures, namely, that the difference in the diffusivities peculiar to the two colours is much reduced when they are simultaneously transmitted by the same retinal area, although it is still present to some degree, as

the behaviour of the flicker photometer shows. This apparent mutual action does not, however, appear to occur between the photopic and the after-images. The latter behave as though due to an entirely separate mechanism.

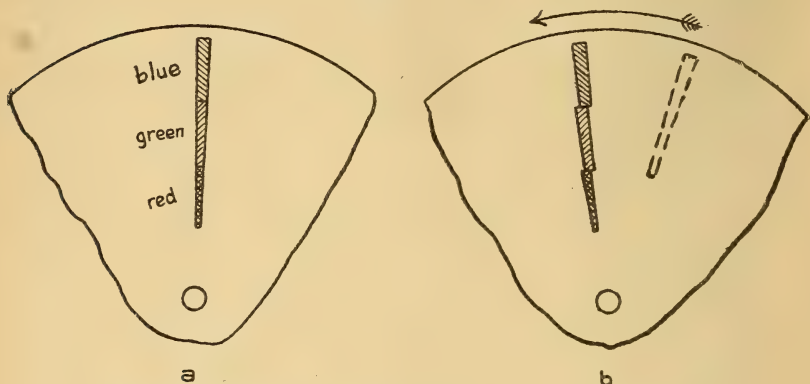
(e) *After-images.*

The most characteristic feature of the positive after-image, if it actually is not a recurrent impression, but the slowly transmitted impression through the rods, as the present theory would indicate, would be that the interval between it and the photopic image would be variable with the intensity. With decreasing intensity the after-image should move in towards the blue image, and at very low intensities should merge into it.

Another characteristic of this after-image would be that, in accordance with the well-established wave-length sensibility of the eye for scotopic vision, the red end of the spectrum is practically inoperative—that is, there should be no after-image of a red stimulus.

These phenomena are all exhibited by providing the slots with red, green, and blue glasses, in the manner indicated in fig. 6 *a*. On rotation the three colours are shifted out of line, in accordance with the subject-matter of the previous sections, and at some distance behind the green and blue

Fig. 6.



Appearance of red, green, and blue apertures lying in straight line:
a, stationary; *b*, in motion.

images—but not behind the red—is the colourless after-image, the after-images of the two colours appearing in the same straight line, as they should from the theory. The appearance at this stage is as shown in fig. 6 *b*. On decreasing the

intensity the after-image moves in closer ; at rather lower intensity the after-image appears merely as a grey tail to the green and blue images ; while at the very lowest intensities these latter become single grey images.

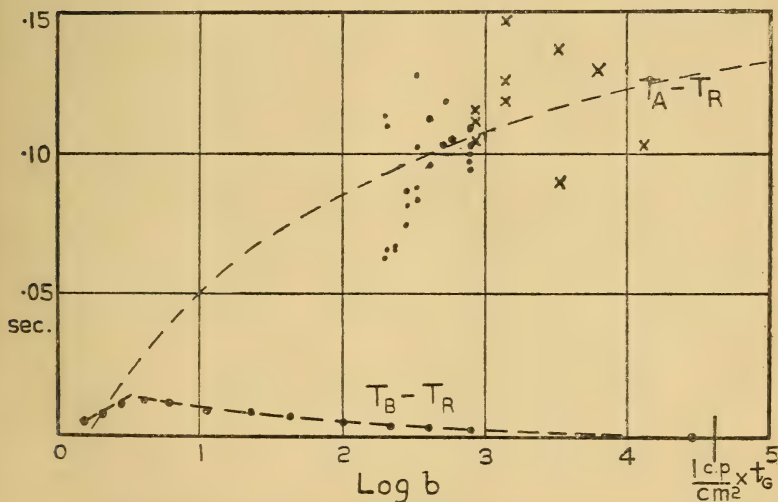
An observation worthy of record, though probably not new, is that the after-image when only slightly separated from the blue primary image is distinctly the brighter of the two.

4. Measurements.

(a) Instrumental conditions and constants.

For the greater part of the measurements the rotating sector disk was illuminated by a tungsten lamp of approximately 100 candle-power, mounted on an eight metre photometer track to permit of a wide variation of illumination by variation of distance. The brightness of the opal glass without any colour screen was one candle per square centimetre at the point marked on the arbitrary logarithmic scale of fig. 7. The photometric transmission

Fig. 7.



Experimental results. Time-intervals between blue and red image perceptions, and between after and red image perceptions.

of the red and blue glasses used over the opal glass was nearly the same, probably not far from five per cent. for the high brightness conditions. The relative brightness of

course varied greatly with the illumination, due to the Purkinje phenomenon.

It is of considerable importance that the eye be properly fixated at the centre of rotation of the disks. The best means found for insuring this was to faintly illuminate the chalk-marked centre of the axle by a beam of light from a distant light and mirror.

The observations were made by the chief observer in a carefully darkened booth. Speeds of rotation were regulated by an adjustable resistance in series with the disk motor. Speeds were read and lamp positions changed by an assistant*.

In this work the artificial pupil heretofore consistently used was omitted because it was found that, owing to the chromatic aberration of the eye, slight unavoidable eye-movements cause relative movements of the red and blue images similar in appearance to those due to the diffusivity differences, and hence likely to be confused with them in measurement.

(b) *Measurements on red and blue light.*

No measurements were made on two lights of different intensity (case 1 above), as the case of two colours practically includes it, and is more striking and easily measurable, because of the approximate equality of brightness which may be arranged for in the two colours under observation.

A series of values of the time-interval between the red and blue light used, for different illuminations, is shown in fig. 7. In making this series the angle between O_A and O_B was one degree at the higher intensities and two degrees at the lower. The employment of larger angles and hence higher speeds, which would at first thought appear preferable, was actually found to be rather less conducive to accuracy because the images begin to spread out and so lose in definiteness of outline.

The predicted behaviour of the two colours with respect to each other is borne out by the measurements.

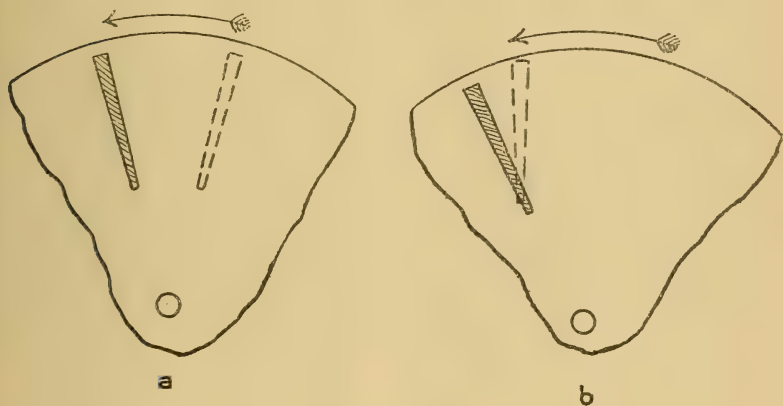
(c) *Measurements on after-images.*

Measurements on the positive after-image, or slowly transmitted rod image as it is here considered to be, are extremely difficult. Two kinds of difficulty may be mentioned—those of fixation and those of visibility. It is absolutely necessary, if accurate measurements are to be

* Acknowledgment is due Mr. E. R. Morton for assistance in the experimental work.

made, that the eye be steadily fixed at the centre of rotation of the disks. If the eye follows the image, as its tendency is, because of the faintness of the phenomenon, the after-image is shifted forward, by an amount which can entirely vitiate the measurement. The manner in which this shift occurs is rather interesting, as it shows clearly that the eye-ball does not rotate, but keeps its axis parallel as it follows the bright spot on the disk. The after-image thus does not merely move in closer, but appears to stand at an angle to the primary image, and if the eye-movement is rapid enough it may actually lie diagonally across this, as shown in fig. 8.

Fig. 8.



Appearance of after-image (shown dashed); *a*, with proper fixation at centre of rotation: *b*, with improper fixation.

Accurate fixation at the centre of rotation is assured by having this faintly illuminated. With accurate fixation, however, the difficulties due to the low visibility of the image are rather enhanced, for one's attention is distracted from the part of the field in which the after-image appears. From one cause or another the illumination region in which any measurements at all can be made on the after-image is quite limited. Thus at a rather high illumination the after-image disappears entirely, as though the rods ceased to function. At an illumination somewhat below this the after-image is fairly bright, and well separated from the primary at moderate speeds. It is here at its best visibility. From here down it becomes less bright, at the same time moving in toward the primary, both changes reducing its visibility. A faint image close to a bright one, whatever

the nature of the objects, is hard to see, especially when in motion. An increase of speed, which would increase the separation, is no aid because of the spreading out and loss of definition of both images. As a consequence the after-image practically disappears, especially as a measurable thing, until at very low illuminations the primary (blue) image becomes, as noted, of the same order of brightness as the after-image, when the latter again appears close in, but, because of the low brightness, not easily susceptible of exact measurement.

A further obstacle to measurement is the fact that the eye quickly loses its ability to see the after-image, and must be rested. This does not appear to be at all a matter of adaptation, in particular of dark adaptation, but of time alone. It was found by experience that the eye was best prepared by an interval between observations of fifteen or twenty minutes at least of use in ordinary occupations of reading, &c., in the normally day-lighted room. Probably under these conditions the rod function is completely inhibited and permitted to recuperate, whereas at the illuminations where both primary and after-image are present this same function is being more rapidly exhausted than its normal rate of recuperation under conditions of pure rod vision.

The measurements obtained are shown in fig. 7. The dots were observations made with the tungsten lamp, as described above, the after-image being brought into coincidence with the red image of the other aperture placed from ten to twenty degrees behind. The crosses represent observations made with an arc lamp with both apertures blue, a condition presenting some advantage at those intensities where the red aperture becomes decidedly brighter in appearance than the blue, due to the Purkinje effect. All observations are, however, reduced to give the interval between red and after-image, by use of the blue-red interval previously determined for the same conditions. It will be seen that these observations, limited in range and lacking in precision for the reasons given, are in agreement, so far as they go, with the hypotheses presented as to the nature of the after-image. They are not sufficient in range or precision to prove it, and so its chief support must be in the qualitative observations described above.

In an effort to find conditions of easier visibility for the after-image a different form of apparatus was improvised, consisting of two white strips carried on an axis like the hands of a clock. One of these was turned through an angle

of ten to twenty degrees, and the two then rotated together until the after-image of one appeared in line with the other. The advantage of this apparatus was that the eye could be much more easily kept fixated at the centre of rotation, half of the phenomenon of interest being on each side of the centre. In the apparatus constructed illumination was necessarily from the front, which made it difficult to have a perfectly black background; perhaps substantially better results could be obtained with a similar device arranged for transmitted light, for the improvement in ease of fixation is considerable. However, there was no indication that the gap between high and low illumination conditions would be appreciably better filled by this scheme, so that the construction of such an apparatus was not undertaken.

Some observations made with this clock-hand device, using white light*, indicated a bending back or return of the after-image just before its disappearance at the highest illumination. This might be due to a failure of the rectilinear logarithmic relation between diffusivity and illumination, such as some earlier work on critical frequency suggested, or again it might be due to the rod function showing a tendency to increase its diffusivity just before failure. The clock-hand observations differed in magnitude from the ones plotted, but in the opposite direction to what better fixation would have accounted for, probably due to the different part and area of retina used.

5. *Discussion.*

The lagging of a blue image after a red is such a striking sight that it seems unlikely to have escaped observation, although I can find no mention of it. As an effect predicted from a physical theory of the transmission of impressions from the retina to the seat of consciousness it may, I think, claim novelty.

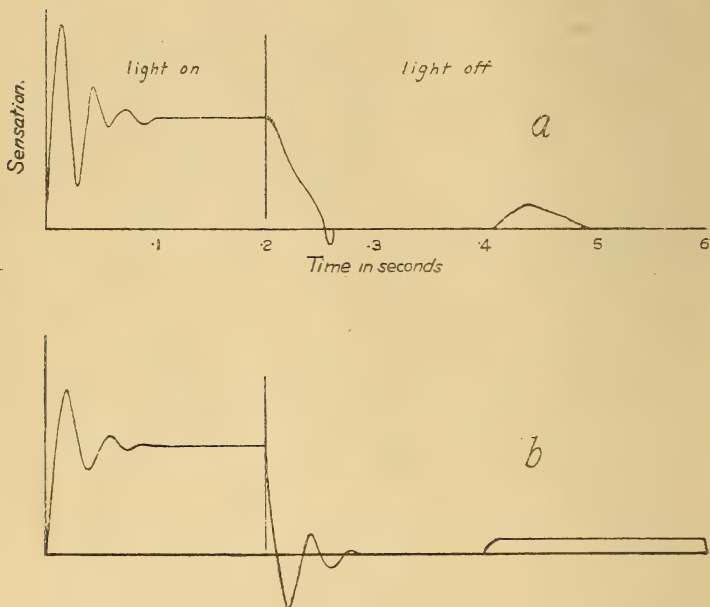
The positive after-image has, of course, been known for a very long time, and it is, moreover, a part of von Kries's *Duplicitäts-theorie* that this image is the rod image, delayed in perception by the greater reaction time of the rods. The existence of a relationship between the illumination and the time-interval separating the after-image from the primary, such as is here suggested and in part borne out, appears to be new.

* When the white hands are illuminated by the yellow-white light of the tungsten lamp, the after-image appears blue; if a blue glass is placed over the eye the after-image appears brown, pointing clearly to the colour being a subjective contrast effect.

Some of the interesting experiments described by Shelford Bidwell * would, with very slight modifications, have shown all the effects which form the subject-matter of this paper. One of his experiments, for instance, was the rotation of a spectrum about an axis beyond the red end. The different apparent positions of the various colours probably escaped him owing to their gradual transition one into another, while a crude artificial spectrum of several patches of colour would have revealed the peculiarity. The curved after-image which he shows following the spectrum I believe has that shape due to imperfect fixation, as illustrated in fig. 8, or perhaps to its extending over a sufficient extent of the retina to show a probable variation of diffusivity from centre to periphery.

One of Bidwell's diagrams, illustrating the fluctuating intensity of the extended image of a rotating bright slit

Fig. 9.



- a.* Progress of sensation with time due to a $\frac{1}{5}$ second exposure according to Bidwell: *b*, electrical transmission of brief stimulus by line containing inductance and capacity.

and its after-image, deserves attention in any discussion of the visual processes as in part phenomena of physical transmission. This diagram, produced in fig. 9*a*, is to be compared with fig. 9*b*, which is the record of a brief

* Bidwell, Proc. Roy. Soc. lvi. 1894, p. 132.

contact as transmitted by an electrical transmission line containing inductance and capacity. The similarity is very striking, especially if we add the delayed record of a second line of high resistance, constituting the after-image.

The postulation of inductance and capacity for the transmitting media in vision is, of course, a considerable step in advance over the simple type of diffusivity which is sufficient to handle the brief exposure and intermittent phenomena. The oscillatory character of the image as described by Bidwell may just as well be ascribed to an oscillatory photo-chemical reaction, of which several are known. At the same time the very great light thrown on these transient visual effects by treating them as physical transmission phenomena will, I think, entitle visual "diffusivity" to a place of some importance in future theories of vision.

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III. *The Vapour Pressure of Zinc, Cadmium, and Mercury.* By A. C. EGERTON *.

IN a quest for a method to determine the vapour pressures of various solid elements, it was attempted to employ a process similar to that which has been used by L. Pfaundler (*Ann. d. Phys.* (3) lxiii. p. 36, 1897) and others, but the results did not promise to lead to a satisfactory general method. Subsequently Professor Nernst drew my attention to Knudsen's † work on the vapour pressure of mercury, and it has been found possible to adapt his method to the determination of the vapour pressures of other elements.

The following is an account of the determinations of the vapour pressure of zinc, cadmium, and mercury. It is hoped to continue the investigations for other elements and, by comparing the results obtained for different elements, to gain a measure of the forces between the atoms. The results for these elements already show that that hope is well founded. In 1909 Knudsen published an account of the determination of the vapour pressure of mercury by a method which depended on his investigations of the kinetic flow of molecules through small apertures and tubes. The apparatus consisted of a glass tube, separated into two compartments by a thin

* Communicated by Prof. H. L. Callendar, F.R.S.

† *Ann. d. Phys.* (4) xxix. p. 179 (1909).

glass partition having in the centre a small aperture. Mercury was placed in one compartment and kept at a constant temperature, the other was kept cool; the vapour of the mercury flowed through the aperture and condensed in the cool portion of the tube.

The amount (G) which condensed was weighed after a certain time (T), and the difference of pressure of the mercury in the two compartments at the constant temperature 0°C. is given by

$$p - p' = \frac{(w_1 + w_2)G\sqrt{\rho}}{T},$$

where $w_1 + w_2$ is the resistance offered to the passage of the vapour by the hole and tube, and ρ is the density of the vapour.

The "resistance" of the aperture, if the walls are quite thin, is given by $w_1 = \frac{\sqrt{2\pi}}{A}$, where A is its area. While the "resistance" of the tube is found from the relation

$$w_2 = \frac{3\sqrt{\pi}}{8\sqrt{2}} \int_0^L \frac{o_1}{A_1} dl,$$

where L is the length from aperture to condensation point, o_1 is the circumference of the tube, and A_1 the cross-sectional area of a length dl of the tube.

Knudsen measured the area of his small irregular apertures by means of a Zeiss Abbé "Zeichen apparatus" and planimeter. In order to simplify the method, tubes have been constructed with accurately circular holes, the diameter of which could be measured by a micrometer. This was also done with a view to increasing the sensitiveness of the method by increasing the number of holes drilled in the plates, so that measurements of pressures of even a millionth of a millimetre of mercury could be made.

2. Experimental.

The following forms of tube have been employed in this work.

Glass Tubes.—Apertures about 2 mm. Diameter of tube 2–3 cm. Length 20 cm. These were standardized by first determining by their means known vapour pressures of mercury at certain temperatures.

Tubes with platinum plate.—These gave good results with

mercury, and were used in order to investigate the method employing a number of holes. Cadmium alloys readily with platinum, and so these tubes could not be used with that metal.

Tubes with iron plate.—The thin steel plates in which holes are drilled are mounted in iron collars ground flat to a glass flange inside the tube. If necessary, the iron collar is cemented with magnesia and silicate paste to the glass flange. These tubes do not give such accurate results unless the collar is well-cemented to the glass flange.

Fused quartz with ground cap.—This is the form of the apparatus which is of most general application. Messrs. Johnson and Matthey succeeded in boring accurately circular apertures in very thin silica for me. Apertures of different sizes and number can then be mounted on silica caps which are ground to fit the silica tube. With such tubes, it will now be possible to determine the vapour pressures of many other metals, such as lead, tin, &c.

In Knudsen's experiments, the mercury was condensed on the sides of the tube by the cooling agent, and afterwards shaken down into a small calibrated tube. In the following experiments carried out on the vapour pressure of mercury for the purpose of standardizing the glass tubes, the mercury pellet was always weighed directly.

In the case of the experiments on cadmium a different method of deposition of the metal was used. The end of the tube possessed a ground joint, through which passed a glass tube and on to this was sealed the end of a thin test-tube. The inside of the tube was cooled by a stream of water. The cadmium deposited on the outside of this thin cooled tube. In order to make sure of the "resistance" of the tube under such circumstances, the tubes were standardized with mercury, allowing the vapour to condense on the same tubes cooled with liquid air.

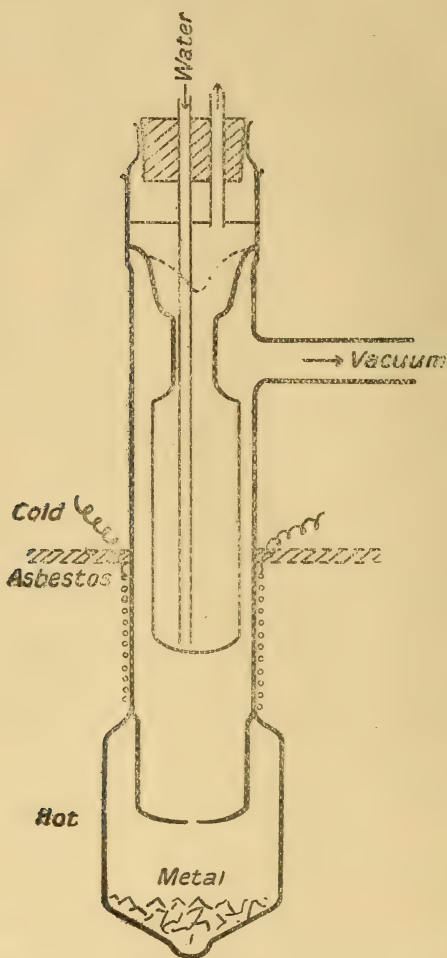
The chief object of such a method was to obtain the deposit so that it could be easily weighed. The end of the glass tube is cut off after the experiment and weighed; the deposit is then dissolved off and the tube weighed again.

There are some objections to this method, and it has been found better, on the whole, to allow the vapour to condense on the walls of the tube, keeping them cool outside. This can only be done when the metal deposits in such a way that it flakes off easily without loss; the tube has to be detached from the apparatus at the end of the experiment, the deposit being then scraped off and collected. Both methods have

been employed in this work, and on the whole the latter has proved the more satisfactory.

It is a matter of some difficulty to maintain fairly high temperatures constant over long periods of time. Vapour

Fig. 1.



baths and baths of high boiling liquids were both found unsuitable for various reasons above 200° . Below this point, a very satisfactory oil-thermostat electrically heated and controlled was used. Above this temperature, an electrically heated air-bath was employed. It was controlled electrically

by means of a relay connected to a mercury thermometer with a large bulb, and stirred by an asbestos fan. All six sides of the uralite box were wound with spirals of resistance-wire. The box was carefully insulated by means of slag wool packed round between it and a large wooden box outside. A box of this description could be kept automatically at a constant temperature throughout within $0^{\circ}5$ C.; but when the tubes are inserted, the leakage of heat up the tubes caused the temperature to fluctuate. In order to overcome this difficulty, the tubes themselves were wound outside closely with resistance-wire, for three or four centimetres, between the position of the hole and the point of deposition. This circuit was operated by the same relay and the heating so regulated by a resistance, that it just counteracted the leakage up the tube.

The temperature itself was measured by mercury thermometers, standardized and corrected for stem exposed. No doubt further refinement would be obtained by the use of resistance-thermometers, but this complication has been left for subsequent work.

Another important point is the maintenance of a good vacuum. In the experiments with mercury, Knudsen recommended washing the tubes out with hydrogen, so as to be sure that the residual gas did not interfere with the accuracy of the results, by colliding with the molecules of vapour in their passage through the aperture. In the preliminary experiments on mercury made in Professor Nernst's laboratory (Berlin), the precaution was taken to boil the mercury in a separate tube. After sealing the latter and the main tube from the mercury pump, the mercury was then tipped into the main tube and the side tube was sealed off.

In the case of the experiments with such metals as cadmium or zinc, or when metals such as iron are employed for the materials in which the hole is bored, it is necessary to keep a "good" vacuum throughout the experiment. This was accomplished by means of a charcoal tube kept in liquid air. The gas which is evolved is chiefly carbon oxides and water vapour; the trace of hydrogen has not been found to be sufficient to cause detriment to the experiments.

Besides this, a Rose oil-pump was found very convenient for quickly obtaining a high vacuum: in some of the shorter experiments, it was found best to fill the tube with nitrogen, insert it in the baths, and when the temperature was constant, to quickly pump out the nitrogen; the time of starting in this way could be reduced to one minute.

Weighings were made on a balance sensitive to 0.02 mg.

Detail of Experiments.—In Table I. are to be found the results of the preliminary experiments with mercury. Tubes A and B were made of glass with a platinum partition

TABLE I.

| Platinum Plates. | | | | Mercury. | | | | |
|----------------------|-------|--------|-------------------------|--------------------|-------------|------------|------------------|-------------------------|
| Tube. | Time. | Weight | Area of Hole. | Length to Deposit. | Resistance. | Temp. ° C. | Vapour Pressure. | Remarks. |
| A..... | 2370 | 0.7867 | 0.0335 cm. ² | 6.5 cm. | 80.46 | 33.7 | 0.00399 | Heated by Ether Vapour. |
| A..... | 2360 | 0.7157 | „ „ | 10.0 „ | 83.8 | 33.8 | 0.00377 | |
| B..... | 2160 | 0.6755 | 0.0328 „ | 9.0 „ | 84.57 | 34.3 | 0.00392 | |
| B..... | 2730 | 0.8283 | „ „ | 8.7 „ | 84.21 | 34.05 | 0.00386 | „ „ |
| A..... | 2317 | 0.1328 | 0.0335 „ | 8.7 „ | 82.6 | 15.5 | 0.000646 | Thermostat. |
| E..... (17 Holes) | 697 | 1.9105 | 0.699 „ | 6.0 „ | 8.98 | 34.2 | 0.00366 | „ |
| E..... (17 Holes) | 2844 | 0.4193 | „ „ | 7.0 „ | 9.5 | 0.0 | 0.000189 | Ice-Bath. |
| E..... (17 Holes) | 1878 | 2.7652 | 0.699 „ | 9.0 „ | 11.68 | 28.6 | 0.00253 | Thermostat. |
| E..... | 2617 | 2.6247 | „ „ | 8.5 „ | 11.0 | 24.9 | 0.00179 | „ |

having a circular hole in the centre. Tube E had 17 circular holes. Before sealing on the platinum plates, the holes were accurately measured. In the case of the plate with many holes, a photographic enlargement was made, a standard centimetre being enlarged at the same time. The experiments show that, although the accuracy is decreased in the latter case owing to the small resistance of the hole, smaller vapour pressures can be determined by multiplying the number of holes. Knudsen's correction for the tube's

resistance, viz. $\frac{3}{8} \frac{\sqrt{2}}{\sqrt{\pi}} \int_0^2 \frac{o_1}{A} dl$, appears to hold satisfactorily.

Experiments were undertaken at various times to standardize the glass tube C, the tube F with iron plate, and the other tubes G and H,—these results are given in Table II. The first experiments with tube C were made in exactly the same way as the experiments with the platinum plates, the mercury being heated in the upper portion of the apparatus in a vapour-bath of ether. The other experiments

TABLE II.

| Tube. | Time. | Weight. | Length to deposit. | Temperature. | Vapour Pressure. | Resistance. | Estimated Mean. | Remarks. |
|--------------------------|--------|---------|--------------------|--------------|------------------|-------------|-----------------|--|
| C (glass),..... | 1878 | 0.4855 | 11.5 cm. | 28.6 | 0.00247 | 63.2 | 63.1 | Mercury deposited on outer Tube. |
| C " | 2617 | 0.4658 | 11.0 " | 24.9 | 0.00182 | 63.0 | } | |
| C " | 250.5 | 0.0452 | 4.2 " | 22.72 | 0.001517 | 59.4 | 61.9 | Mercury deposited on inner Tube cooled by liquid air. |
| C " | 254.0 | 0.04397 | 5.2 " | 22.72 | 0.001517 | 63.0 | | |
| C " | 245.25 | 0.11720 | 5.2 " | 35.1 | 0.00416 | 61.7 | | |
| C " | 427.0 | 0.19766 | 5.2 " | 35.4 | 0.00418 | 63.8 | | |
| C " | 426.5 | 0.20267 | 5.2 " | 35.4 | 0.00418 | 61.9 | } | |
| C " | 400.0 | 0.05898 | 5.2 " | 21.0 | 0.00126 | 61.9 | | |
| F (iron plate) | 252.0 | 0.03255 | 6.3 " | 22.72 | 0.00151 | 84.9 | 88.6 | Mercury deposited on inner Tube cooled by liquid air. Iron plate probably not making good contact. |
| F " | 255.0 | 0.03189 | 4.9 " | 22.72 | 0.00151 | 87.2 | | |
| F " | 246.5 | 0.07850 | 4.9 " | 35.1 | 0.00416 | 92.6 | | |
| F " | 428.0 | 0.1418 | 4.9 " | 35.4 | 0.00418 | 89.2 | | |
| F " | 425.5 | 0.14797 | 7.5 " | 35.4 | 0.00418 | 85.0 | } | |
| F " | 399.5 | 0.03854 | 7.5 " | 21.0 | 0.00126 | 94.5 | | |
| F " | 307.5 | 0.10264 | | 34.1 | 0.00380 | 80.6 | 83.6 | Mercury deposited on inner Tube. |
| F " | 240.0 | 0.08518 | 7.4 " | 35.2 | 0.00416 | 83.2 | | |
| F " | 444.0 | 0.1510 | 7.4 " | 35.2 | 0.00416 | 86.9 | } | Iron plate cemented down. |
| G (glass),..... | 307.0 | 0.12428 | 5.2 " | 35.2 | 0.00416 | 66.4 | 66.2 | Mercury deposited on inner Tube. |
| G " | 379.5 | 0.16972 | 5.2 " | 35.2 | 0.00416 | 66.0 | } | |
| H (iron plate, 9 holes). | 455.0 | 0.04021 | 5.8 " | 198.5 | 0.000275 | 13.4 | 14.0 | On inner Tube. |
| H " | 455.0 | 0.02659 | 7.1 " | 199.0 | 0.000280 | 14.3 | } | On outer Tube Oil thermo-stat. |

were made later in the course of the work ; the purpose was to make certain of the "resistance" of the tube when an internal cooled tube was used on which to deposit the metal. The mercury was condensed out by keeping the inner cooling tube filled with liquid air. It is noticeable that the mercury condenses as an opaque dark film on the cooled tube ; opaque, although when warmed and melted there is often no trace of mercury on the tube visible to the naked eye.

Although this way of calibrating the tube is not so accurate as the former method, it is very useful in obtaining the necessary correction for w_2 the "resistance" of the tube. w_1 can be measured directly in the case of the iron tube. It is found that the resistance of the tube is increased somewhat by the presence of the inner tube, as one would be led to expect. The lower value $w_1 + w_2 = 83.6$ for the iron tube gives vapour pressures which are in good agreement with the values for the vapour pressure obtained in the experiments with cadmium using the glass tube C ; this is additional evidence of the validity of the figure for the resistance of the tube F.

It would have been quite sufficient to have only considered the values obtained with tube C in the cadmium experiments. Tube F was employed partly to check and add additional weight to the results with tube C, and partly to further investigate the use of the iron-plate type of tube, so that plates with many holes could be constructed and utilized for later experiments.

In an experiment with the large tube (3 cm. diameter) H with iron plate of 9 holes, the holes were first measured and the tube also standardized in the oil-bath at 200° and found to agree with the measured values, if the requisite measurement of length of tube is made for calculating w . Considering the smallness of the vapour pressure, measurements down to 150° C. were made fairly satisfactorily. But two experiments at 140° C. and 128° C. gave no measurable result. It is noteworthy that Krafft*, working with cathode-ray vacuum, and also Demarçay† mention that at about 150° the vapour pressure of cadmium suddenly becomes undetectable.

The experiments with zinc were first of all carried out with tube C, in order to investigate roughly the lie of the curve. In the meantime, however, Messrs. Johnson and

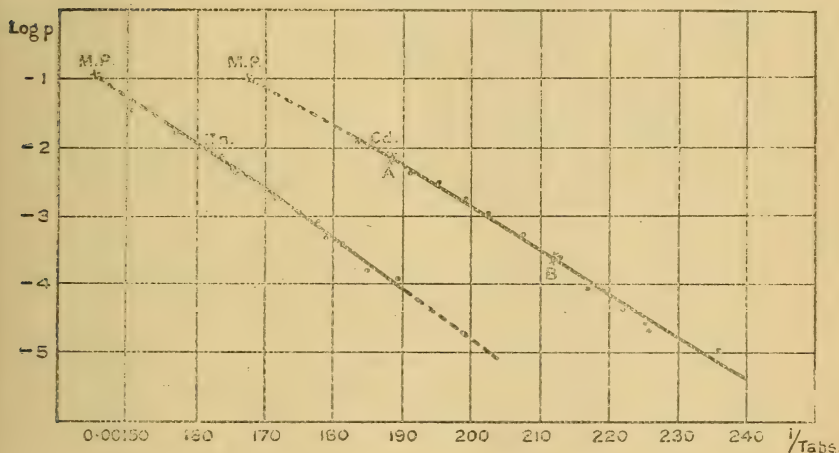
* Krafft, *Ber. Deut. Ges.* 1903 A, vol. xxxvi. p. 1690 ; 1905 A, vol. xxxviii. p. 254.

† Demarçay, *Comptes Rendus*, vol. xcv. p. 183 (1882).

Matthey succeeded in making the silica tubes for me. Tube A (Si) was similar to the glass tube C, except that it was made after the circular hole was measured. Tube B (Si) possessed two ground caps, as already described, the apertures of which were carefully measured.

Two points on the curve (see fig. 2) for cadmium were checked, using the two silica tubes, and for the higher point

Fig. 2.



the smaller hole was used in connexion with tube Si B, while for the lower one the larger hole cap was placed in position. It is very satisfactory that the results of the two sets of experiments agreed so well, as with tubes of different kinds, any uncertainty in the correction for length and standardization of the tube must have shown itself. The two higher points obtained are shown at A on the curve, and the lower ones at B.

The experiments which have so far been carried out show that the method is capable of general application, and it is hoped that it may be possible to continue the experiments for other metals. At very low pressures it appears that the metal does not condense satisfactorily, and results are not as accurate as was hoped for. The reason may either be due to collision with traces of residual gas, or to repeated reflexion without condensation from the walls of the tube. It has been noticed that metal condenses and grows in a patch or streak, as if when it strikes the clean

glass it is not at once condensed but undergoes a series of reflexions. It is also noticed that it is more readily condensed on itself. In support of this, in some experiments it has been found that the cadmium condenses in separate sticky grey molecules or filaments, which are seen to be composed of a number of small irregular crystals when viewed under the microscope. Further, it has already been mentioned that mercury condensed by the aid of liquid air forms an opaque black film on the condensing surface, which becomes practically invisible on warming to atmospheric temperature. The mercury coalesces on warming.

It might be possible to attain better results at very low pressures by cooling to a lower temperature, or by using a tube on which metal is already condensed and which has been carefully weighed. At pressures above 10^{-4} mm., the repeated reflexions do not affect the results, as a comparatively large difference of pressure on either side of the aperture is maintained.

The zinc deposit is a beautiful bluish-white lustrous film, but if the quantity is very small it generally presents itself as a grey powder. The cadmium deposit is considerably greyer in colour, but beautifully lustrous. For a small quantity, the powdery form is yellowish grey. The deposit is streaky and appears to follow streaks in the glass or silica. The metals condense on the walls of the tube in a band of about $1\frac{1}{2}$ cm. in breadth on that portion of the tube as it emerges from the hot-box. There is a distinct and fairly narrow region of greatest thickness when the deposit is obtained on a cooled inner tube, the end of the tube opposite the hole is sometimes left bare, showing that reflexion occurs to a considerable extent; the thickest part of the deposit is just where the tube becomes straight. There is also generally a small deposit on the walls of the tube. In all cases the shape of the deposit is such that the straight line emission demonstrated by Dunoyer is exhibited; in one experiment with a narrow condensing tube it has been noticed that the metal deposited in bands of distinctly different thickness, as if particles of different range were being condensed. Many interesting points arise in an investigation of the condensation of these metals, but it is a study apart from the scope of this paper*.

* Prof. R. W. Wood, in an interesting paper (Phil. Mag. xxxii. p. 364), has recently made a study of the subject which bears out the above observations.

3. Results.

The results which have been obtained could no doubt be represented in a similar manner to that of mercury (liquid) with a formula of the Rankin type, or the Biot type.

For mercury Knudsen found

$$\log p = 10.5724 - 0.847 \log T - \frac{3342.26}{T}.$$

But since the vapours of these metals have proved to be monatomic, it is worth while to find out how closely the results agree with the formula derived from the Clausius equation :

$$\lambda = RT^2 \frac{d \ln p}{dT}$$

and $\lambda = \lambda_0 - (C - Cp)T$, where C is the molecular heat of solid, and Cp is the molecular heat of the vapour at constant pressure; whence

$$\ln p = -\frac{\lambda_0}{RT} - \left(\frac{C - Cp}{R}\right) \log T + \text{constant};$$

but assuming * $C - Cp = 3R - \frac{5}{2}R = \frac{R}{2}$;

hence

$$p = K \cdot T^{-\frac{1}{2}} e^{-\frac{\lambda_0}{RT}}.$$

It is found that for cadmium

$$p = 5.27 \cdot 10^{13} T^{-\frac{1}{2}} e^{-\frac{2.77 \cdot 10^4}{RT}} \text{ dynes per sq. cm.,}$$

or

$$\log p = 10.5979 - 0.5 \log T - \frac{6060}{T} \text{ (mm.).}$$

For zinc,

$$p = 1.17 \cdot 10^{14} T^{-\frac{1}{2}} e^{-\frac{3.28 \cdot 10^4}{RT}} \text{ dynes per sq. cm.,}$$

or

$$\log p = 10.9443 - 0.5 \log T - \frac{7176}{T} \text{ mm.}$$

Hence for cadmium $\lambda_0 = 2.77$, whereas on calculation according to the formula of Nernst,

$$\lambda_0 = TB \cdot 8.5 \log T_B,$$

the latent heat of vaporization

$$\lambda_0 = 2.70.$$

* The value of λ_0 calculated in this way cannot be taken as quite correct, as the assumption with regard to specific heats is not true. When due allowance for the changes of specific heat has been made, the values of k , λ_0 , and the index of T will probably be slightly different; but by assuming the index of T to be $-\frac{1}{2}$, the simplest approximation is obtained, wherewith to compare the results obtained for the different elements.

| Exp. | Tube. | Sample Cd. | Time. | Weight grain s. | Length to hole from deposit. cms. | Length of deposit. cms. | Resistance w_1, w_2 . | Mean Temp. |
|----------|--------------|------------------|-------|-----------------|-----------------------------------|-------------------------|-------------------------|------------|
| 8 | C | <i>b</i> | 1550 | 0·04612 | 6·0 | ... | 61·9 | 208·5 |
| 9 | (abandoned). | | | | | | | |
| 10 | C | <i>b</i> | 2705 | 0·09840 | 9·0 | 5·0 | 62·2 | 210·0 |
| 11 | C | <i>b</i> | 1300 | 0·04650 | 6·0 | 3·5 | 61·9 | 210·5 |
| 12 | C | <i>b</i> | 1800 | 0·06426 | 5·5 | 3·0 | 61·9 | 209·2 |
| 12 | F | <i>c</i> | 1800 | 0·04894 | 9·7 | 2·5 | 83·6 | 209·2 |
| 13 | C | <i>b</i> | 1309 | 0·13610 | 5·7 | 4·0 | 61·9 | 228·5 |
| 13 | F | <i>c</i> | 1309 | 0·09670 | 10·0 | 2·0 | 85·7 | 228·5 |
| 14 | C | <i>b</i> | 1384 | 0·13840 | 12·5 | 2·5 | 64·3 | 228·5 |
| 14 | F | <i>c</i> | 1384 | 0·11320 | 6·0 | 2·0 | 83·6 | 228·5 |
| 15 | C | <i>b</i> | 1240 | 0·07047 | 6·0 | 10·0 | 61·9 | 220·2 |
| 15 | E | <i>c</i> | 1240 | 0·05493 | 9·0 | 9·0 | 85·0 | 220·2 |
| 16 | C | <i>b</i> | 930 | 0·06335 | 6·0 | 3·0 | 61·9 | 221·5 |
| 16 | E | <i>c</i> | 930 | 0·04868 | 6·0 | 3·0 | 83·6 | 221·5 |
| 17 | C | <i>b</i> | 494 | 0·15370 | 6·0 | ... | 61·9 | 248·9 |
| 17 | F | <i>c</i> | 494 | 0·10971 | 6·0 | 1·4 | 83·6 | 248·9 |
| 18 | C | <i>b</i> | 1020 | 0·19382 | 6·0 | 3·0 | 61·9 | 239·7 |
| 18 | F | <i>c</i> | 1020 | 0·14524 | 6·0 | 3·0 | 83·6 | 239·7 |
| 19 | C | <i>b</i> | 2040 | 0·00300 | 6·0 | 3·0 | 61·9 | 178·0 |
| 19 | F | <i>c</i> | 2040 | 0·00546 | 6·0 | 3·0 | 83·6 | 178·0 |
| 20 | C | <i>b</i> | 1354 | 0·02342 | 6·0 | 3·0 | 61·9 | 197·5 |
| 20 | F | <i>c</i> | 1354 | 0·01782 | 6·0 | 3·0 | 83·6 | 197·5 |
| 21 | C | <i>b</i> | 2990 | 0·00149 | 7·0 | 1·5 | 61·9 | 168·5 |
| 21 | F | <i>d</i> | 2990 | 0·00350 | 6·5 | 1·5 | 83·6 | 168·5 |
| 22 | C | <i>b</i> | 254 | 0·22106 | 6·0 | 4·0 | 61·9 | 271·0 |
| 22 | F | <i>d</i> | 254 | 0·15731 | 5·5 | 3·5 | 83·6 | 271·0 |
| 23 | C | <i>b</i> | 2600 | 0·01466 | 6·0 | 2·0 | 61·9 | 188·5 |
| 23 | F | <i>d</i> | 2600 | 0·01209 | 5·5 | 2·5 | 83·6 | 188·5 |
| 24 | C | <i>b</i> | 240 | 0·12527 | 6·0 | 2·0 | 61·9 | 259·5 |
| 24 | F | <i>d</i> | 240 | 0·09928 | 5·5 | 2·5 | 83·6 | 259·5 |
| 25 | SiA | purest | 352 | 0·13261 | 9·9 | 2·0 | 82·3 | 260·0 |
| 25 | SiBi | „ | 352 | 0·07429 | 6·5 | 2·0 | 138·0 | 260·0 |
| 26 | SiA | „ | 1339 | 0·02048 | 10·8 | 2·0 | 83·0 | 200·5 |
| 26 | SiB2 | „ | 1330 | 0·01775 | 7·8 | 2·5 | 87·9 | 200·5 |
| 29 | H | <i>e</i> iron | 1588 | 0·01415 | 7·2 | 1·5 | 14·0 | 170·6 |
| 30 | H | <i>e</i> plate | 11420 | 0·03152 | 7·0 | 2·0 | 14·0 | 150·5 |
| 31 | H | <i>e</i> 9 holes | 8405 | 0·00030 | 7·6 | 1·5 | 14·0 | 140·0 |

III.

| Corrected Temp. | Reciprocal Temp. abs. | Vapour Pressure. | $\log p$. | Remarks. |
|-----------------|-----------------------|----------------------|------------|---|
| 208.8 | 2.075 | $4.35 \cdot 10^{-4}$ | -3.361 | { First exp. after the addition of wire. Test of method of scraping down deposit. |
| 210.4 | 2.068 | $5.35 \cdot 10^{-4}$ | -3.271 | |
| 210.8 | 2.0660 | $5.24 \cdot 10^{-4}$ | -3.280 | { Deposit on walls. Vacuum not very good, deposit on tube. |
| 209.5 | 2.0720 | $5.22 \cdot 10^{-4}$ | -3.282 | |
| 209.5 | 2.072 | $5.36 \cdot 10^{-4}$ | -3.270 | Dep. on tube. |
| 229.2 | 1.991 | $1.55 \cdot 10^{-3}$ | -2.809 | Dep. on walls. |
| 229.2 | 1.991 | 1.53 „ | -2.815 | Dep. on tube, glossy. |
| 229.5 | 1.990 | 1.55 „ | -2.809 | Dep. on walls. |
| 229.5 | 1.990 | 1.65 „ | -2.782 | { Dep. on walls, some deposit lost (.0005 gram). |
| 220.7 | 2.025 | $8.40 \cdot 10^{-4}$ | -3.075 | |
| 220.7 | 2.025 | 8.99 „ | -3.046 | Dep. on tube. |
| 222.0 | 2.020 | $1.01 \cdot 10^{-3}$ | -2.998 | Dep. on walls. Spread about. |
| 222.0 | 2.020 | 1.05 „ | -2.979 | Dep. on tubes. Scraped off. |
| 249.9 | 1.912 | 4.73 „ | -2.324 | Dep. on tubes (rather oxidized). |
| 249.9 | 1.912 | 4.56 „ | -2.340 | Dep. on tube. |
| 240.5 | 1.947 | 2.88 „ | -2.540? | Dep. on tube. |
| 240.5 | 1.947 | 2.90 „ | -2.537 | Dep. on tube. |
| 178.2 | 2.216 | $2.08 \cdot 10^{-5}$ | -4.682 | { Dep. in "sticky" form on walls and end tube. |
| 178.2 | 2.216 | 5.11 „ | -4.291 | |
| 197.7 | 2.125 | $2.50 \cdot 10^{-4}$ | -3.602 | { Vacuum not good. Good deposit, a little lost (0.0005 gram). |
| 197.7 | 2.125 | 2.56 „ | -3.592 | |
| 168.7 | 2.264 | $6.97 \cdot 10^{-6}$ | -5.156 | Good deposit. Temp. doubtful. |
| 168.7 | 2.264 | $2.21 \cdot 10^{-5}$ | -4.656 | On tubes. |
| 272.5 | 1.833 | $1.35 \cdot 10^{-2}$ | -1.869 | New Cd. |
| 272.5 | 1.833 | 1.30 „ | -1.886 | On tubes. Temp. doubtful. |
| 188.7 | 2.165 | $8.06 \cdot 10^{-5}$ | -4.093 | { On tubes. |
| 188.7 | 2.165 | 8.98 „ | -4.046 | |
| 260.8 | 1.873 | $8.02 \cdot 10^{-3}$ | -2.096 | { Started and stopped with N ₂ . |
| 260.8 | 1.873 | 8.59 „ | -2.066 | |
| 259.4 | 1.878 | 7.80 „ | -2.108 | |
| 259.4 | 1.878 | 7.45 „ | -2.127 | |
| 198.7 | 2.119 | $2.96 \cdot 10^{-4}$ | -3.528 | |
| 198.7 | 2.119 | 2.72 „ | -3.564 | |
| 169.0 | 2.261 | $2.82 \cdot 10^{-5}$ | -4.550 | |
| 148.8 | 2.361 | 1.10 „ | -4.959 | |
| 138.2 | 2.431 | $1.0 \cdot 10^{-7}$ | | |

TABLE IV.

| Tube. | Sample Zn. | Time, mins. | Weight, grams. | Length to hole from deposit, cms. | Length of deposit. | Resistance $w_1 + w_2$. | Mean Temp. | Corrected Temp. | Reciprocal abs. Temp. | Vapour Pressure. | log p . | Remarks. |
|---------|------------|-----------------------|----------------------------|-----------------------------------|--------------------|--------------------------|------------|-----------------|-----------------------|----------------------|-----------|--|
| C | <i>a</i> | 180 (less) 1413 | 0.0105 (low) 0.01471 | 5.7 | 3.0 | 61.9 | 297.5 | -300.5 | 1.743 | $1.22 \cdot 10^{-3}$ | -2.914 | { Leak; time doubtful. Good shiny blue. |
| C | <i>a</i> | | | 5.2 | 3.0 | 61.9 | 266.4 | 268.0 | 1.848 | $1.73 \cdot 10^{-4}$ | -3.762 | { Deposit on inner tube. Temp. doubtful. Deposit possibly some lost? Deposit some on walls, black. |
| C | <i>a</i> | 386 | 0.09064 | 5.5 | 2.5 | 61.9 | 326.4 | 330.4 | 1.657 | $5.03 \cdot 10^{-3}$ | -2.298 | { |
| G | <i>b</i> | 1140 | 0.02659 | 5.8 | 3.0 | 66.2 | 287.5 | 285.9 | 1.789 | $5.15 \cdot 10^{-4}$ | -3.288 | { Vacuum not good. Deposit uneven. Tube G was broken. |
| SiA ... | <i>c</i> | 1539 | 0.11623 | 10.8 | 6.5 | 83.0 | 310.7 | 311.7 | 1.714 | $2.13 \cdot 10^{-3}$ | -2.672 | On walls rather spread. |
| SiA ... | <i>c</i> | 1490 | 0.04573 | 10.2 | 3.0 | 82.3 | 290.7 | 291.4 | 1.772 | $8.44 \cdot 10^{-4}$ | -3.0735 | Good deposit. |
| SiA ... | <i>c</i> | 262 | 0.06998 | 11.2 | 5.0 | 83.0 | 339.6 | 341.3 | 1.679 | $7.73 \cdot 10^{-3}$ | -2.112 | Deposit spread about. |
| SiA ... | <i>c</i> | 2865 | 0.01286 | 10.3 | 3.0 | 82.3 | 256.3 | 256.8 | 1.888 | $1.20 \cdot 10^{-4}$ | -3.921 | Grey deposit. |
| SiA ... | <i>c</i> | 1245 | 0.01906 | 11.0 | 3.0 | 83.0 | 280.0 | 280.0 | 1.808 | $4.21 \cdot 10^{-4}$ | -3.376 | { Grey deposit. Temp. rather irregular, regulated by hand. |
| SiA ... | <i>c</i> | 222 | 0.13744 | 11.0 | ... | 83.0 | 360.5 | 363.0 | 1.571 | $1.82 \cdot 10^{-2}$ | -1.740 | |
| SiA ... | <i>c</i> | 400 | 0.07504 | 11.0 | ... | 83.0 | 331.2 | 332.7 | 1.651 | $5.39 \cdot 10^{-3}$ | -2.268 | |

For zinc, $\lambda_0 = 3.28$, instead of 3.12 from the empirical formula. The theoretical formula, therefore, agrees with the observed results remarkably well.

From the empirical formula for mercury given by Knudsen:

$$\log p = 10.5724 - 0.847 \log T - \frac{3342.26}{T},$$

the value of λ for the liquid given by the Clausius equation would be $1.51 \cdot 10^4$ cal. at the melting-point, where the vapour pressure would become $2.0 \cdot 10^{-6}$ mm. The latent heat of fusion has been determined by Bridgeman (Amer. Acad. Proc. xlvii. no. 12, pp. 347-438), and at the melting-point the value is $5.6 \cdot 10^2$ cal.; hence the heat of sublimation of the solid would be $1.57 \cdot 10^4$. If the equation $\lambda_T = \lambda_0 - (C - C_p)T$ were to hold over the range to absolute zero, λ_0 would become $1.61 \cdot 10^4$ cal. Inserting the value 1.60 in the equation for the vapour pressure and assuming the vapour pressure to be $2.0 \cdot 10^{-6}$ mm. at the melting-point, the equation

$$p = 3.72 \cdot 10^{13} \cdot T^{-\frac{1}{2}} e^{-\frac{1.60 \cdot 10^4}{RT}} \text{ dynes per sq. cm.}$$

is obtained.

The following table gives the results for these elements, the first two columns give the value of λ as calculated by Nernst's empirical equation and the corresponding value of the constant K, and the next two columns the values of λ_0 and K obtained from the observations of the vapour pressure, expressed by the equations given above.

| | λ . | K. | λ_0 . | K. | Absolute B.-Pt. | Absolute M.-Pt. | Molecular latent heat of Fusion. |
|------------|-------------------|----------------------|-------------------|----------------------|-----------------|-----------------|----------------------------------|
| Zinc | $3.12 \cdot 10^4$ | $2.9 \cdot 10^{13}$ | $3.28 \cdot 10^4$ | $1.17 \cdot 10^{14}$ | 1191° | 691° | $1.82 \cdot 10^3$ |
| Cadmium... | $2.70 \cdot 10^4$ | $2.63 \cdot 10^{13}$ | $2.77 \cdot 10^4$ | $5.27 \cdot 10^{13}$ | 1051° | 594° | $1.57 \cdot 10^3$ |
| Mercury... | $1.50 \cdot 10^4$ | $4.41 \cdot 10^{12}$ | $1.60 \cdot 10^4$ | $3.72 \cdot 10^{13}$ | 630° | 234°·2 | $5.6 \cdot 10^2$ |

* *I. e.* $\log p = 10.4466 - \frac{1}{2} \log T - \frac{3500}{T};$ and

extrapolating to a value at 0° C. for the vapour pressure of solid mercury, the value would be $2.56 \cdot 10^4$ instead of $1.86 \cdot 10^4$ for the liquid.

The angle of slope of the vapour pressure curve for mercury is slightly less than half that of the slopes of the zinc and cadmium curves, which are very similar. The values of $\frac{dp}{dT}$ at the melting-points of the three elements are:

$$Z_n \ 4.41 \cdot 10^{-3} \text{ mm.}$$

$$\text{Cd } 3.70 \cdot 10^{-3} \text{ mm.}$$

$$\text{Hg } 2.81 \cdot 10^{-7} \text{ mm.};$$

while at a point of equal pressure $2.0 \cdot 10^{-6}$ mm.,

Zn $1.25 \cdot 10^{-7}$ mm. at the temperature 502° absolute,

Cd $1.39 \cdot 10^{-7}$ mm. „ „ 436° „

Hg $2.81 \cdot 10^{-7}$ mm. „ „ 234° „

At the melting-point the vapour pressures of zinc and cadmium appear to be very nearly equal (Zn $1.13 \cdot 10^{-1}$ mm.; Cd $1.0 \cdot 10^{-1}$ mm.). The physical constants for these three elements are remarkable in that zinc and cadmium closely resemble each other, while the constants for mercury have throughout a very much smaller value.

It should be possible to link the constants obtained from the vapour pressure formula corrected for the real change of specific heats with the tensile strength and other elastic constants, and so obtain data for the measurement of the forces of cohesion and of the law of attraction and repulsion between atoms. This work was in hand when other more pressing duties forced it to be placed aside nearly two years ago.

It was not intended to publish the results before finishing the above calculation, but it is now thought advisable to publish the experimental results as they stand. I am indebted to Professor Strutt and Professor Callendar for having allowed me to proceed with this work at the Imperial College, South Kensington.

August 1915.

IV. *Energy Distribution in Spectra.*—I. By R. T. BEATTY, M.A., D.Sc., Lecturer in Physics, The Queen's University of Belfast*.

[Plate II.]

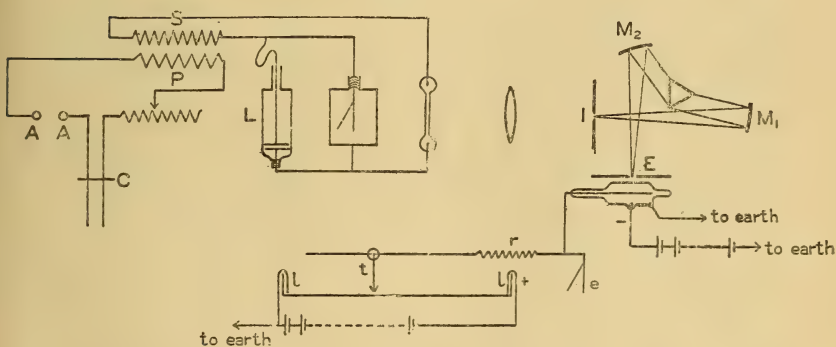
[The expenses of this investigation have been partly defrayed by grants from the Government Grant Committee of the Royal Society and from the Institut international de Physique Solvay.]

IN this paper the author describes an investigation of the energy emitted by the lines of the spectrum of hydrogen in the visible region. The light from a Geissler tube was analysed by a monochromator, and its intensity was measured by a photo-electric cell which was calibrated by means of a carbon filament glow-lamp.

The Production of the Light.

A Gramme machine was fitted with two slip-rings connected to two opposite points of the armature-winding, so that when the machine was excited by a direct-current dynamo supplying current at 60 volts it acted as a rotary converter, giving alternating current with a frequency of about 40 alternations per second. The terminals A A (fig. 1)

Fig. 1.



were connected to this source of alternating supply. The current passed through the primary P of an induction-coil and a variable rheostat, and a fine adjustment could be made by sliding a copper bar C along two parallel resistance wires. In the secondary circuit the induced high potential current passed through the secondary S of the induction-coil, the Geissler tube, and the liquid resistance L consisting of a mixture of copper sulphate and glycerine.

* Communicated by the Author. A preliminary account of this work was given in a paper read before Section A of the British Association at its Newcastle Meeting, September 1916.

The liquid resistance was contained in a glass tube whose uniform portion was 26 cm. long and 2.5 cm. internal diameter. The electrodes were two parallel copper disks, the lower one fixed, while the upper could be raised or lowered by a vertical copper rod screwed into the disk.

When the electrodes were at their greatest distance apart the resistance between them was 4.3×10^4 ohms, and the resistance for intermediate positions was determined, so that any desired value could be obtained by altering the position of the movable electrode.

One electrode was also connected to the gold leaf of a Wilson tilted electroscope and the other to the case and brass plate inside. The position of the gold leaf was observed through a microscope, with a scale in the eyepiece which was so arranged that when a difference of potential of 130 volts existed between the case of the electroscope and the gold leaf, the latter was focussed on the zero of the eyepiece scale.

The current through the Geissler tube was accordingly to be calculated by dividing this difference of potential by the resistance of the liquid between the copper electrodes. To obtain a given current these electrodes were set at the proper distance apart, and the primary current adjusted till the image of the gold leaf coincided with the zero of the microscope-scale. The current was kept constant by an observer who controlled the sliding copper bar while looking into the microscope.

The tube became hot during the passage of the discharge, and in order to prevent the pressure of the gas from changing, a bulb of 1 litre capacity was sealed on as described by Guild*. This arrangement also diluted any gaseous impurities which might be given off by the electrodes or glass walls of the tube. Nevertheless, it was found that the intensities of the spectrum-lines increased with time when a steady current was maintained, nor was it possible to attain to a final steady condition†. Accordingly a clockwork arrangement was included in the primary circuit, so that the current was on for six seconds and off for fourteen. In this way the tube was kept in a constant condition, and readings could be repeated time after time in a satisfactory manner. The advantage of using an electroscope to measure the current now became strikingly evident. The motion of the gold-leaf is dead-beat, and the position of equilibrium is

* Phys. Soc. Proc. xxviii. pp. 60-71, Dec. 1915.

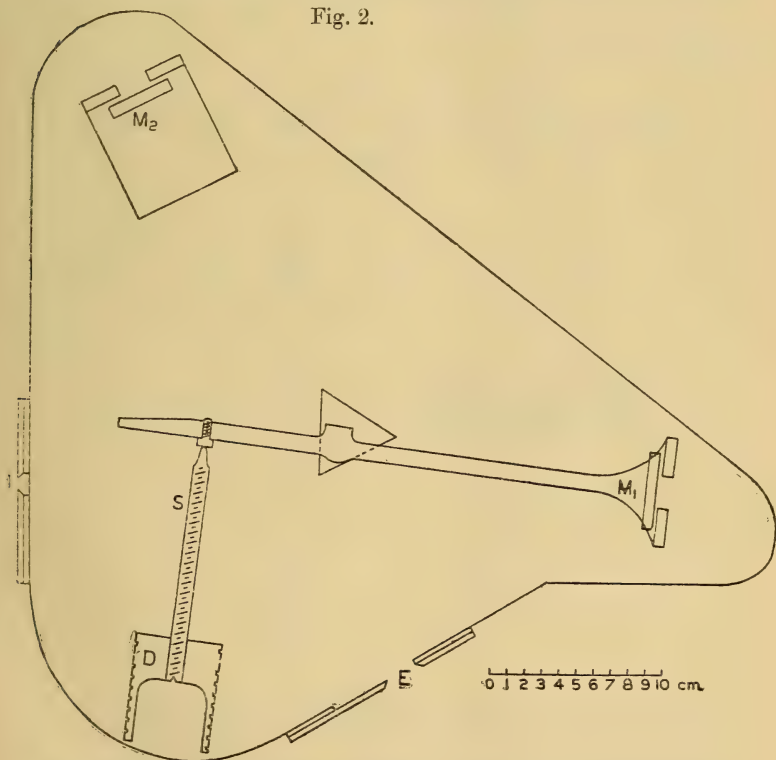
† A reference to fig. 9 will give the explanation of this phenomenon. The heated gas in the Geissler tube will have a density equivalent to cold gas at a lower pressure. Hence if the gas is at a pressure greater than 1.3 mm. the intensities of the lines will increase corresponding to a movement along the curve in the direction of decreasing pressure.

attained in a fraction of a second; so that the observer could satisfy himself that the current was of the proper magnitude during the brief space of six seconds allowed him. A thermammeter requires several seconds to reach its final position, so that for the purposes of this research an expensive milliammeter would have been actually less satisfactory than the simple arrangement here described.

The Monochromator.

This instrument was designed by Mr. John Wylie, B.A., of the Physics Department, and was constructed in the laboratory workshop. Light focussed on the incidence-slit I (fig. 1) was rendered parallel by reflexion from the concave mirror M_1 and dispersed by a dense glass prism of 60° angle.

Fig. 2.



The dispersed beam was reflected from the concave mirror M_2 , and the spectrum focussed in the plane of the slit E. M_1 and the prism were rigidly mounted on a horizontal steel arm which was pivoted below M_1 , and could be moved by the rotation of a screw S (fig. 2) attached to a drum D.

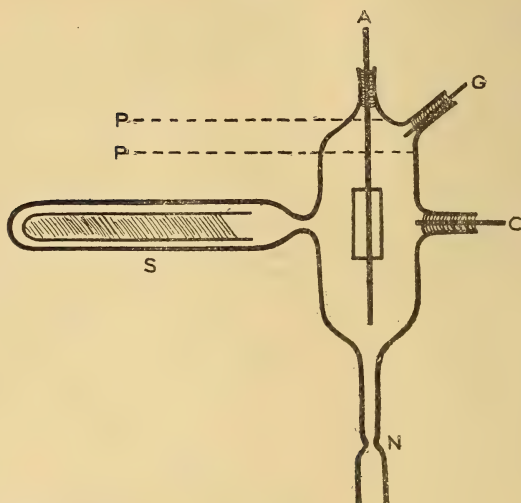
Monochromatic light could thus be made to issue from the emergence slit E in the position of minimum deviation. The drum was engraved on its outer circumference with a scale of wave-lengths from 3800 to 8000 Å.U., the calibration being carried out by observation of many well-known lines in the spectrum. The essential parts of the instrument are drawn to scale in fig. 2. E was shaped to the average curvature of the spectrum-lines so as to obtain as much light as possible, and the jaws of the slit could be removed to allow of a photographic plate being mounted when desired. The mirrors were silvered by cathode deposit, and could easily be removed for re-silvering.

The Geissler tube, the condensing lens, and the monochromator were mounted on an optical bench. I was usually opened to admit about $5\ \mu\mu$, and E to admit about $7\ \mu\mu$ of the spectrum.

The Photo-Electric Cell.

A tube* of fused quartz (fig. 3) was provided with three

Fig. 3.



electrodes, whose points of entry were made air-tight by the use of lead seals. The anode A is an aluminium rod, 2 mm. diameter, fused on to the molybdenum wire which passes through the quartz. C is the cathode and G a guard electrode. The interior of the tube was thickly silvered,

* This tube was made and the electrodes sealed in by the Silica Syndicate, Hatton Garden, London.

and a guard-ring was made by scraping away the silver in the planes through the dotted lines P P at right angles to the axis of the tube. The silver deposit was also removed to leave a rectangular window 20×4 mm. in the side of the tube. A side tube S containing a mixture of rubidium chloride and calcium was then fused on, and the whole apparatus was exhausted by a Gaede pump. During exhaustion the apparatus was heated by a Bunsen burner to remove films of gas from the walls.

S was then raised to a cherry-red heat, whereupon the rubidium chloride and calcium reacted, setting free the rubidium*, which distilled over and formed a coating on the walls of the cell. This coating was driven off the window and the narrow strips of surface on each side of the guard-ring by local heating with a small pointed gas-flame. S was then sealed off at the constriction and helium was admitted to the cell at a pressure of a few millimetres, so that a luminous discharge could be made to pass between the cathode and the anode (the former being in metallic connexion with the inner wall of the tube) under a pressure of 200 volts. The cell was then finally sealed off at the constriction N.

In order to increase the sensitiveness by obtaining the colloidal modification of rubidium, the narrow end of the cell was raised to a white heat in a blowpipe-flame, to allow a small quantity of hydrogen to diffuse into the cell. On passing a discharge the hydrogen rapidly combined with the rubidium. This process was repeated till the metallic lining, which was previously silvery white, became appreciably blue. In this way, as Elster and Geitel discovered, the sensitiveness in the selective region is greatly increased.

The photo-electric currents given by this cell per unit amount of energy falling on the incidence slit are shown in fig. 10. It will be seen that the selective region of wave-lengths to which rubidium is most sensitive covers the visible spectrum, but the addition of potassium and caesium would probably diminish the rapid drop which occurs towards the blue and red wave-lengths.

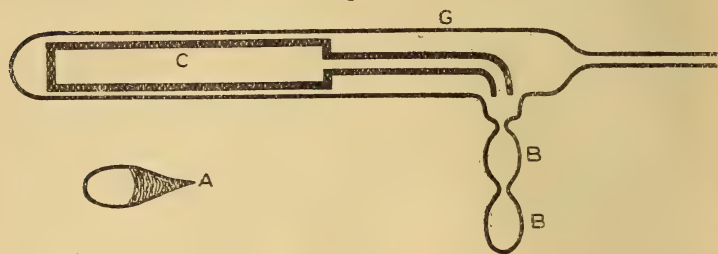
The advantages of quartz as compared with glass in the construction of the cell are: (1) observations can be taken in the ultra-violet, (2) the mixture from which rubidium is to be generated can be heated in a side tube without risk of collapse, (3) in the preliminary heating of the cell there

* This method of reducing alkali metals from their chlorides was first described by J. Hackspill. *Comptes Rendus*, cxli. p. 106 (1905).

is no possibility of fracture due to sudden changes of temperature.

In constructing a glass cell the rubidium must be prepared beforehand. The method found most suitable is shown in fig. 4. C is a copper vessel fitted with a narrower copper

Fig. 4.



tube bent at the end. The vessel is filled with the mixture of calcium and rubidium chloride, and a copper end-piece screwed on. It is then placed inside the glass tube G, which is afterwards closed at one end. The apparatus is connected to a Gaede pump, and when exhausted the tube around C is carefully heated. At a red heat the softened glass shrinks on to C, but remains intact as long as the high temperature is maintained. The rubidium vapour is delivered by the bent tube and drops collect in the side tube. By gentle heating the rubidium is made to flow into the bulbs B B, which are then sealed off.

The design of a glass cell is the same as that of the quartz one shown in fig. 3, except that the electrodes are fused in the ordinary way. A bulb A (fig. 4), containing rubidium, has the tip of the drawn-out end broken off, and is then inserted in the side tube S (fig. 3). After closing the end of S and exhausting, the metal is transferred to the cell by gentle heating. Only the small surface of metal closing the narrow end of the bulb becomes oxidized, so that the greater part of the rubidium remains available.

Method of using the Photo-electric Cell.

The cell was placed with the window close in front of the emergence slit of the monochromator (fig. 1). The cathode was connected to the negative end of a set of small accumulators, so that its potential was about two volts less than that required to produce a luminous discharge in the helium. The anode was connected to the gold-leaf of a double quadrant

electroscope* e , so that a negative current of electricity flowed to the leaf when light entered the cell.

The electroscope was used as a null instrument. To effect this, arrangements were made to balance the photo-current by a current of positive electricity, so that the leaf should remain at zero potential. The method used is shown in fig. 1. A rectangular glass tank ll 100 cm. long, 6 cm. deep, and 1 cm. wide was filled to a height of 2.5 cm. with a mixture of saturated copper sulphate and glycerine. Copper electrodes were inserted at each end, that on the left being earthed, the other kept at a potential of +40 volts. An insulated vertical copper tongue t dipped in the liquid and was mounted on horizontal rails so that it could travel the whole length of the tank. This tongue was connected to the gold-leaf through a high resistance r of 6.87×10^{11} ohms†.

Hence if x be the distance in cms. between the tongue and the left-hand electrode, the potential of t is $\frac{x}{100} \times 40$ volts, and the current flowing to the gold-leaf (which we suppose earthed for the moment) is

$$\frac{x}{100} \times 40 \times \frac{1}{6.87 \times 10^{11}} \text{ amperes :}$$

that is, the current is proportional to x .

Hence if the tongue be moved so that this current just balances the photo-electric current, the latter amounts to $x \times 5.83 \times 10^{-13}$ ampere. Observations were taken by moving the tongue till the gold-leaf was at zero potential, the photo-current being then proportional to the reading of the tongue in cms.

Intensity Ratios in the Balmer Series of Hydrogen.

Pure H_2O vapour was admitted to the Geissler tube and the pressure measured by an oil-gauge. An alternating current of 15 milliamperes was passed through the tube, and the photo-currents due to H_α , H_β , H_γ , H_δ measured. The observations were repeated at various pressures with the

* Beatty, Phil. Mag. Nov. 1907, p. 606.

† This resistance was made by depositing platinum by cathode discharge on a quartz rod 1 cm. long, whose ends were copper plated and soldered to copper wires, the whole being contained in an evacuated glass tube. The apparatus was made three years ago (Beatty, Proc. Roy. Soc. A. lxxxix. 1913, p. 318), and its resistance has increased since then from 5.57×10^{10} ohms to 6.87×10^{11} ohms.

same current, and the results are shown in Table I. Fig. 5 (Pl. II.) is plotted from the last three lines of Table I., and shows the intensity ratios as functions of the pressure. The ratio for any two lines remains constant till the pressure falls below a given value, and then the lines with the higher ordinal numbers in the Balmer series become relatively more intense. The photo-currents due to H_δ were very small, and the curve showing H_δ/H_γ is not very trustworthy.

TABLE I.
Water Vapour.

| p in mm. | | ·4 | ·6 | ·8 | 1·0 | 1·2 | 1·4 | 1·6 | 1·8 | 2 | 3 | 4 | 6 | 8 | 10 |
|-----------------|-----------------------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| Photo-Currents. | H_a . | 7·4 | 8·5 | 9·2 | 9·7 | 9·8 | 9·8 | 9·7 | 9·6 | 9·35 | 7·6 | 6·0 | 4·2 | 2·9 | 2·2 |
| | H_β . | 86 | 91 | 92 | 94 | 92 | 88 | 80 | 77 | 73 | 51 | 39 | 27 | 18 | 14·1 |
| | H_γ . | 5·9 | 5·9 | 5·8 | 5·8 | 5·5 | 5·2 | 4·6 | 4·2 | 3·9 | 2·2 | 1·7 | 1·15 | ·77 | ·59 |
| | H_δ . | ·83 | ·71 | 5·8 | ·70 | ·55 | ·47 | ·50 | ·38 | ·39 | ·20 | ·15 | ·15 | ·08 | ·051 |
| | H_β/H_a . | 11·6 | 11·7 | 10·0 | 9·7 | 9·4 | 9·0 | 8·3 | 8·0 | 7·8 | 6·7 | 6·4 | 6·4 | 6·2 | 6·4 |
| | H_γ/H_β . | ·069 | ·065 | ·063 | ·062 | 0·60 | ·059 | ·057 | ·056 | ·054 | ·043 | ·044 | 0·42 | ·043 | ·042 |
| | H_δ/H_γ . | ·14 | ·12 | ·10 | ·12 | ·10 | ·09 | ·11 | ·09 | ·10 | 0·9 | ·09 | ·13 | ·11 | ·08 |

Similar experiments were made with pure dry hydrogen admitted through a heated palladium-platinum tube fused into the glass. A side tube furnished with silver electrodes was sealed on and a discharge passed so as to form a silver deposit on the walls. When fresh, this deposit rapidly absorbs mercury vapour*, the green and yellow mercury lines disappearing in the course of half-an-hour. The many-line spectrum of hydrogen was now prominent, and it was necessary to allow for it in measuring the intensities of the Balmer lines.

Table II. gives the results obtained with and without the background to which the many-line spectrum gives rise. Fig. 6 (Pl. II.) shows the intensity ratio H_β/H_a in the latter case. The upward bend of the curve at low pressures takes place as with water vapour.

Fig. 7 (Pl. II.) shows the photo-currents obtained with water vapour at a pressure of 8 mm. Fig. 8 (Pl. II.) illustrates the corresponding curve with pure dry hydrogen

* This excellent method of eliminating mercury vapour was suggested to the author by Mr. T. R. Merton, B.Sc., King's College, London.

(free from mercury vapour) at 4.63 mm. In the latter case the background contributes such a large portion of the total intensity in the vicinity of H_γ and H_δ that the ratios δ/γ and γ/β have not been shown in fig. 6, as the numbers were not sufficiently reliable.

TABLE II.

Pure dry Hydrogen free from Mercury Vapour.

| <i>p</i> in mm. | ·127 | ·526 | 1.1 | 3 | 4 | 6 | 8 |
|-------------------------|------|------|-----|-----|-----|-----|-----|
| A. H_β/H_α . | 25 | 11.6 | 5.8 | 4.7 | 4.4 | 4.0 | 4.8 |
| B. H_β/H_α . | 13.1 | 9.4 | 8.9 | 9.3 | 9.0 | 8.5 | 9.2 |

A. Intensity Ratios with background subtracted.

B. Intensity Ratios including background.

Discussion of the Intensity Ratios.

The Rutherford * hydrogen atom consists of a nucleus with a single unit positive electric charge and an electron with an equal negative charge. According to Bohr's † theory of spectra, the electron may rotate in any one of a series of circular orbits round the nucleus, the radii of consecutive orbits or rings being as the squares of the natural numbers. When the electron passes from ring 3 to ring 2 the atom emits the red line H_α . Similarly, in passing from rings 4, 5, 6, to ring 2 the lines H_β , H_γ , H_δ , respectively, are emitted. The atom may pass from its normal condition into any one of these states by collision with a free electron which possesses a certain amount of energy. Expressing this energy in terms of the potential difference in volts through which the free electron must fall to acquire it, we have the following relation between n and the energy absorbed by the atom in reaching the different ring configurations

$$E = 13.6 \left[\frac{1}{1^2} - \frac{1}{n^2} \right].$$

TABLE III.

E = energy absorbed by atom in volts.

n = number of ring in which the hydrogen electron revolves.

| | | | | | |
|---------------|------|------|------|------|------|
| E | 10.2 | 12.1 | 12.7 | 13.0 | 13.6 |
| n | 2 | 3 | 4 | 5 | inf. |

* Rutherford, Phil. Mag. xxi. (1911) p. 669.

† Bohr, Phil. Mag. July, Sept., Nov. 1913, March 1914, Sept. 1915.

Accordingly, by increasing the velocities of the colliding electrons, the relative intensities of the higher members of the Balmer series might be expected to become greater, that is, the relative intensities would be functions of the potential gradient in the capillary of the Geissler tube. This view, however, is not confirmed by an examination of the variation of the potential gradient with pressure. Nutting and Tugman* give the results shown in the second line of Table IV., taken from page 56 of their paper. In the third line I have given the numbers showing the corresponding fall of potential per mean free path of an electron moving in hydrogen at the pressure mentioned.

TABLE IV.

Discharge in Hydrogen : 2.6 mm. capillary.

Current=15 milliamperes.

| | | | | | |
|---------------------------|------|------|------|------|------|
| Pressure in mms. | 0.5 | 1.0 | 2.0 | 3.0 | 8.0 |
| Volts per cm. | 35.8 | 49.5 | 67.4 | 78 | 120 |
| Volts per free path | 6.17 | 4.27 | 2.91 | 2.24 | 1.30 |

From this table we see that the velocity acquired by an electron between successive collisions decreases with increasing pressure, yet no corresponding variation in β/α takes place at pressures greater than 4 mm., as is evident from figs. 5 and 6 (Pl. II.).

From these and other experimental results which will now be mentioned, the author concludes that *the energy distribution in the lines of the Balmer series is independent of the energy of the colliding electron or molecule which strikes the hydrogen atom and causes it to emit these lines.*

Vegard† found that when hydrogen becomes luminous by the impact of canal rays, the intensity ratio β/α is independent of the velocity of these rays and is of the same value as when the emission is in the negative glow of a discharge tube where the excitation is due to cathode rays. It is to be noted that the pressures in these experiments were so low that the time required by a hydrogen atom to describe a free path exceeded the probable duration of its emission of light.

* Bulletin of the Bureau of Standards, (7) i. August 6, 1910, pp. 49-70.

† *Ann. der Physik*, xxxix. p. 111, 1912.

Holtzmark *, using a Wehnelt line cathode, proved that H_β/H_α is independent of the voltage between 52 and 600 volts, and is also independent of the current strength, but changes with pressure.

These results of Vegard and Holtzmark strongly support the conclusion mentioned above. Confirmatory evidence in the case of other spectra appears from the work of McLennan †, who has shown that in the spectra of mercury, cadmium, zinc, and magnesium caused by an electric discharge, the complete spectrum appears suddenly when the exciting electrons attain definite velocities. The author does not wish to exclude the possibility that under certain conditions electrons may possess such energy that they may excite one line only of the Balmer series, but takes the view that in a luminous discharge the great majority of the radiating atoms have been ionized and give out light owing to subsequent recombination. The method of ionization is taken to be immaterial as regards the distribution of light in different wave-lengths during such recombination.

The intensity distribution will, however, be affected by the mean free path of the luminous atom and the nature of the molecules in its vicinity whose fields of force act on it.

It follows from Bohr's theory that the diameter of the hydrogen atom, and hence its mean free path, will vary as the hydrogen electron passes from one ring to another. Table 5 shows the results calculated for hydrogen atoms moving in water vapour at a pressure of 1 mm.

TABLE V.
Luminous Hydrogen atom in Water Vapour.

| No. of Ring | 1 | 2 | 3 | 4 | 5 | 6 | 10 |
|---|----------------------|----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| Diameter of atom in cms. $\times 10^3$ } | 1.34 | 5.36 | 12.06 | 21.4 | 33.5 | 48.2 | 67 |
| Mean free path in cms. at 1 mm. pressure. } | 9.9×10^{-3} | 3.5×10^{-3} | 1.25×10^{-3} | 5.05×10^{-4} | 2.36×10^{-4} | 1.23×10^{-4} | 1.78×10^{-5} |

Let $E_\alpha, E_\beta \dots$ be the energies which would be emitted per unit number of luminous atoms per second in the lines

* *Phys. Zeit.* June 15, 1914, pp. 605-7.

† *Proc. Roy. Soc. A.* xci. pp. 485-492; A. xcii. pp. 305-313, 574-584.

$H_\alpha, H_\beta \dots$ in the capillary of the tube if the pressure were so low that each atom is undisturbed by collisions while radiating. Let $S_\alpha, S_\beta \dots$ be the distance travelled by an atom while emitting $H_\alpha, H_\beta \dots$. We may call such a distance the length of the luminous streak for the line in question. Let $F_\alpha, F_\beta \dots$ be the mean free paths for an atom radiating $H_\alpha, H_\beta \dots$. Let us also suppose that a single collision is enough to destroy the radiating properties of an atom. Then if the pressure is so high that $F_\alpha < S_\alpha, F_\beta < S_\beta$, the energies emitted will be $E_\alpha \cdot F_\alpha/S_\alpha, E_\beta \cdot F_\beta/S_\beta$, and the ratio H_β/H_α will be constant since the variables F_α, F_β are inversely as p . As the pressure is lowered a stage will be reached where $F_\alpha =$ or $> S_\alpha, F_\beta < S_\beta$: the energies emitted at this and lower pressures will be $E_\alpha, E_\beta \cdot F_\beta/S_\beta$, so that H_β/H_α will now increase with diminishing pressure. Similar considerations hold for H_γ/H_β , &c. Accordingly we may explain figs. 5 and 6 (Pl. II.) as follows.

If the mean free paths of two luminous atoms H_α, H_β are less than their respective luminous streaks, the intensity ratio will remain constant. At lower pressures when the free path of one atom is equal to or greater than its luminous streak, the free path of the other remaining less than its luminous streak, the intensity ratio will change.

When the pressure is very low, so that the whole radiation from an atom can take place between collisions, the intensity ratios should again become independent of the pressure. Experiments are now in progress to test this deduction, a Wehnelt cathode being used to produce a bright discharge in water vapour at low pressure*.

The length of the luminous streak for H_α may be calculated from the curves shown in fig. 5 (Pl. II.). The ratio H_β/H_α begins to change at a pressure of about 3 mm. At this pressure

$$F_\alpha = \frac{1.25 \times 10^{-3}}{3} = 4.2 \times 10^{-4} \text{ cm.} \quad (\text{See Table V.})$$

Hence $S_\alpha = 4.2 \times 10^{-4}$ cm. The distance travelled by the luminous atom during one vibration is $\frac{v\lambda}{c}$, where v = velocity

* In preliminary experiments now in progress it has been found that a strongly luminous discharge can be produced if the stream of electrons is concentrated by using a longitudinal magnetic field due to a powerful electromagnet.

of atom, λ =wave-length, c =velocity of light. Putting in the values

$$v = 1.7 \times \sqrt{2} \times 10^5 = 2.4 \times 10^5 \text{ cm./sec.} = \text{mean velocity of a hydrogen atom at } 0^\circ \text{ C.,}$$

$$\lambda = 6.563 \times 10^{-5} \text{ cm.,}$$

$$c = 3 \times 10^{10} \text{ cm./sec.,}$$

we get distance travelled per single vibration =

$$\frac{2.4 \times 10^5 \times 6.563 \times 10^{-5}}{3 \times 10^{10}} = 5.25 \times 10^{-10} \text{ cm.}$$

Hence the number of vibrations performed by the radiating atom

$$= \frac{4.2 \times 10^{-4}}{5.25 \times 10^{-10}} = 8 \times 10^5.$$

A more accurate value could be found by taking the probability distribution of free paths into account, but it is scarcely worth while to perform the laborious quadratures involved until more experimental results have been obtained.

Change of Intensity with Pressure.

In fig. 9 (Pl. II.) are shown the photo-currents due to H_a at different pressures with constant discharge current. The curve is plotted from Table I., line 1.

The maximum effect is produced when $p=1.3$ mm. This maximum may be explained as follows. The light is due to recombination of $+H$ ions with electrons. At low pressures the speed of the free electrons is so great that recombinations in the positive column are infrequent; at high pressures the free path of the H atom is too small to allow of the full radiation being emitted. At high pressures it will be seen that the curve becomes hyperbolic. This would indicate that the number of $+H$ ions recombining per c.c. per second is constant, the radiation consequently varying directly as the free path, and therefore inversely as the pressure. Nutting and Tugman * give a similar curve, using pure hydrogen.

Calibration of the Photo-Electric Cells in Absolute Units.

Benedict † has found that a carbon lamp behaves as a grey body in the visible spectrum, that is, that its energy

* *Loc. cit.* p. 58.

† *Ann. d. Phys.* xiii. 1915, pp. 641-678.

distribution in different wave-lengths is a constant fraction of that emitted by a black body at the same temperature. The author has made use of this result by allowing the light from a definite narrow strip of the spectrum to fall on the cell, and observing the photo-currents obtained when the energy consumption of the lamp was varied. Since, according to Lummer*, the total energy emitted by a carbon lamp follows Stefan's law the electrical energy supplied per second to the filament varies as the fourth power of the absolute temperature. Hence

$$\frac{E}{E_1} = \left[\frac{T}{T_1} \right]^4.$$

The energy distribution of a grey body is given by $c_1 \lambda^{-5} e^{-\frac{c_2}{\lambda T}}$ (Wien's law), hence the logarithm of the ratio of the photo-currents in the two cases is

$$-\frac{c_2}{\lambda} \left[\frac{1}{T} - \frac{1}{T_1} \right].$$

Hence on plotting $\frac{T}{T_1}$ against this logarithm, T being the variable, we get a line whose slope is $\frac{c_2}{\lambda T_1}$.

This was done for a number of wave-lengths between 400 and 660 $\mu\mu$. In every case a straight line was obtained and the values of T_1 thus calculated lay between 1880° and 1920° abs., the deviations from the average being most marked at the wave-lengths to which the cell is least sensitive.

The temperature of the filament at its normal burning voltage was accordingly taken as 1900° abs. It may be noted that the method gives $\frac{c_2}{T_1}$ and not T_1 , so that the results are independent of any uncertainty as to the value of c_2 . The value for the temperature given above was obtained by putting c_2 equal to 1.445.

The energy per unit breadth of spectrum falling on the slit of the monochromator may now be calculated, an arbitrary multiplication factor being involved.

The numbers so obtained must be multiplied by $\frac{\partial \lambda}{\partial \theta}$, the dispersion of the prism, in order to get the corresponding energies which would leave the emergence slit if no losses

* *Electrotechnische Zeitschrift*, xxxiv. Heft 50, 1913, pp. 1428-1449.

due to absorption and reflexion took place. Thus the actual relation between photo-current and wave-length, when the carbon lamp is used, may be employed to work out the curve connecting the wave-length with the photo-current per unit energy incident on slit.

This relation is shown in fig. 10 (Pl. II.), and we are now in a position to express all the previous curves in terms of the energies emitted by the different hydrogen lines.

Figs. 7 E and 8 E (Pl. II.) were thus drawn by changing the photo-current ordinates of figs. 7 and 8 into energy ordinates by the help of fig. 10.

It will be seen that the greater part of the energy is carried by H_α , and a smooth curve joins the ordinates for H_α , H_β , H_γ , H_δ . As the shape of this curve changes with the pressure no attempt has been made to find a relation between energy and wave-length, though at very low pressures where the atoms can radiate their energy completely, such a relation would probably be capable of a simple interpretation.

Jolly * records similar energy curves obtained with a thermopile, but his tubes were excited by an induction-coil with a capacity in parallel with the tube, and so his curves are not comparable with those obtained in the present investigation—they show, however, a general resemblance.

The curves 7 and 8 giving photo-currents as ordinates show the details better than the energy curves 7 E and 8 E; in the latter the large amount of energy in H_α necessitates a small scale of ordinates for the rest of the spectrum.

Indeed, a great advantage of the photo-electric cell is that it can be made very sensitive to the weak lines in the blue and ultraviolet.

The author intends to continue the work by investigating the discharge at low pressures, and also the spectra of hydrogen compounds, such as HCl and H_2S , in order to elucidate further the variations in the energy distribution.

In conclusion, he wishes to express his thanks to Mr. John Wylie, B.A., for valuable help and advice in designing and constructing much of the apparatus used; to Miss Muriel Campbell, B.Sc., for a series of observations to test the properties of the photo-electric cell, and to Mr. E. W. McClelland for assistance in taking the final readings.

* Phil. Mag. (6) xxvi. November 1913, p. 801.

V. *Equipartition of Energy and Radiation Theory.*
 By W. F. G. SWANN, D.Sc., A.R.C.S.*

Introduction.

IT is usually maintained that the theorem of equipartition of energy is a necessary consequence of the application of the so-called "ordinary dynamics" to a system, and further, that an application of the principle to the problem of radiation necessitates the conclusion that Rayleigh's formula $E_{\lambda}d\lambda = 8\pi RT\lambda^{-4}d\lambda$ ought to be true. Though much has been written in this connexion, it has always seemed to the present author that there are several points which require a somewhat closer scrutiny than is usually given, and which concern themselves chiefly with the question as to how far the results to which the theorem leads have really any connexion with the physical phenomena which they are generally considered to represent. The present paper forms a discussion of some of the points involved in this connexion. Since much of what is here written involves ultimately a careful distinction between the results to which the theorem apparently leads and those to which it really does lead, it will perhaps not be superfluous to commence by giving a brief survey of the essentials involved in the theorem.

Remarks on the Proof of the Theorem.

In the first place, it is to be noted that the theorem itself is as follows. Suppose that the system is specified by a large number n of coordinates and a large number, n , of momenta, and that a certain quantity which is constant (the energy), is a homogeneous quadratic function of the coordinates and momenta of such a kind that in it there are no terms involving products of coordinates and momenta. Then, if we separate out from the energy all those squared terms involving coordinates and momenta which do not appear in the energy otherwise than in the said squared terms, and if from these squared terms we pick out two sets P and Q each containing a large number of terms and take the average value in each case, we shall find that the average for the P group is the same as that for the Q group. Each group may if we choose involve some terms from the potential energy and some from the kinetic. The terms "coordinate"

* Communicated by the Author.

and "momentum" need, in the above, have no other significance than that they are quantities which make the Hamiltonian equations true for the system.

Now let us inquire as to how much of the theory is a result of pure mathematics, and how much involves other considerations. In the first place, suppose that, following Jeans, we consider a generalized space of $2n$ dimensions so that each point in the space has $2n$ coordinates. Further, let there be a number of quantities, $E_1, E_2, E_3, \&c.$, each a function of only one of the coordinates, and suppose that *

$$E_1 + E_2 + E_3 + \&c. = \text{constant} = E, \text{ say.} \quad . \quad . \quad (1)$$

Let us imagine a large number of points distributed with uniform density in the generalized space, and let us confine our attention to a region of the space corresponding to values of E between E and $E + dE$. Consider any point in the space, and from its coordinates pick out a large number p . These p coordinates need not be all of the same type, but let us suppose that the quantities $E_1, E_2, E_3, \dots E_p$, corresponding to them are all of the same mathematical form †. In a similar way pick out another group of q coordinates from the coordinates of the point, and again, let all the E 's be functions of the coordinates of the same mathematical form, though the form for the q group need not be the same as that for the p group. Let us in a similar way pick out a group of r coordinates, and so on; then it follows as a purely algebraical fact that relations of the type

$$\delta n_p = A_p e^{-hE} p^\xi d\xi \quad . \quad . \quad . \quad (2) \quad \ddagger$$

$$\delta n_q = A_q e^{-hE} q^\xi d\xi, \quad . \quad . \quad . \quad (3)$$

$\&c.,$

* It is to be noted that no dynamical significance is as yet attached to the coordinates or to the quantities $E_1, E_2, \&c.$

† So that by altering the scale of the coordinates we can reduce the E 's to exactly the same function of the coordinates. Thus for example the condition would be satisfied if, in the p group,

$$E_1 = m_1 \dot{\theta}_1^2, \quad E_2 = m_2 \dot{\theta}_2^2, \quad \&c.,$$

but would not be satisfied if

$$E_1 = m_1 \dot{\theta}_1^2, \quad E_2 = a \dot{\theta}_2^3.$$

‡ The equations are usually given in a form expressing the number of systems having values of the different coordinates between ξ_1 and $\xi_1 + d\xi_1$, ξ_2 and $\xi_2 + d\xi_2$, $\&c.$, a sort of differentiation in kind being maintained in this way between the coordinates. So long* as the E 's for a particular group, for example the p group, are the same function of their respective coordinates for all coordinates of the group, mathematically the coordinates may be treated as of the same type, even though physically they may be different.

or relations infinitely nearly the same as these, hold for all but an infinitesimal fraction of the generalized space corresponding to the region in question. In these formulæ δn_p represents the number of the coordinates of the p group having values between ξ and $\xi + d\xi$, $E_{p\xi}$ is the contribution to E for the particular value of ξ by a coordinate of the p group, similar remarks applying to the quantities with suffixes q , r , &c. Further, the quantities A_p , A_q , &c., and h are determined by

$$\int \delta n_p = p, \quad \int \delta n_q = q, \text{ \&c.}$$

$$\int E_{p\xi} \delta n_p + \int E_{q\xi} \delta n_q + \dots \text{ \&c.} = E.$$

The important characteristic of equations (2), (3), &c. is that h is the same in all.

If we now go one step farther and restrict E_1 , E_2 , &c., to be proportional to the squares of the generalized coordinates, it follows from (2), (3), &c., that the average value of the E 's for the p terms is the same as that for the q terms or for the r terms, the average value in question being $1/2 h^*$. The theorem at this stage contains all the mathematical law involved in the theorem of equipartition of energy, except that so far there has been no mention of energy or of dynamics. We may give the name energy to the quantities E_1 , E_2 , &c., and of course nothing will be altered, and it remains to inquire what part is played by the Hamiltonian equations, for though the Hamiltonian equations contain the principle of the conservation of energy, the principle of the conservation of energy does not necessitate the Hamiltonian equations.

It will be remembered that if in the generalized space we take the points distributed with uniform density initially, then the law represented by (2), (3), &c., which symbolizes what is called the "Normal State," is found to apply for all but an infinitely small proportion of the points in the domain of the space under consideration. This would obviously have been true if the points had not been chosen uniformly distributed unless in some of the exceptional

* In Maxwell's proof of the theorem, the average is taken not merely over all regions of the generalized space corresponding to the normal state, but over the whole space corresponding to the prescribed energy limits. The reason that the two methods give the same result is of course that so much of the space concerned corresponds to the normal state that the inclusion of the remainder of the space makes no difference to the result.

regions where the normal state did not apply the density of the points happened to be infinitely large*. If we imagine the coordinates in the generalized space to represent the coordinates and momenta of some dynamical system, each point corresponding to a particular state of the system, then, as time progresses, the points will move through the generalized space. The Hamiltonian equations, however, insure that if the density of the points was originally constant, it will, during the motion, remain constant so that there will be no tendency for the points to congregate in those abnormal regions of the space where the normal state does not hold †. This is generally taken to prove that in practice the chance of a system being in an abnormal state is infinitesimal, and it is thus in linking up the mathematical problem with the physical one that the Hamiltonian equations play their part.

The Application of the Theorem.

Arguments of the type summarized above seem to have been accepted largely without question as indicating that the state represented by (2), (3), &c. is infinitely probable in the practical sense. While it would I think be easy to deny the necessity for this conclusion on purely logical grounds, it is perhaps well to supplement the discussion by keeping our minds centred on a particular case so that we may the more readily judge whether objections which we raise against the above conclusions are really pertinent or merely formal.

Let us suppose that we take all the copper in the universe and imagine it divided up into equal blocks ‡ each of which we shall speak of as a system. Let us choose, for examination, those blocks for which the temperature is such that E lies between E and $E + dE$. Now each piece of copper is in a different state, and, having decided what we shall choose as generalized coordinates, suppose that we plot, in the space, points corresponding to each block. We may look upon the

* See J. H. Jeans, "Report on Radiation and the Quantum Theory," p. 34.

† It is worth while observing that the Hamiltonian equations do not necessarily require that the relative configurations of the points shall remain the same throughout the motion. All that is required is that the density shall remain constant. This permits of points becoming thinned out, for example, along the path of a stream line provided that they are crowded to a corresponding extent perpendicular thereto.

‡ More strictly we should say: divided up into blocks each containing the same number of corresponding coordinates.

different blocks as representing different states of the same system. Now there is nothing *a priori* to tell us how the points will be distributed over the region of the space concerned. If they were distributed anything like uniformly, the law represented by (2), (3), &c. would be expected to hold; but if they are not so distributed, it is useless for us to argue as to what would have been expected if they had been so arranged. We must guard against a temptation to expect a fortuitous distribution of the points on the basis that the systems may have been chosen from pieces of copper millions of miles apart, because it may be, and probably would be, that it was just because the coordinates were restricted in some way so as to cause the points to be confined to special regions of the generalized space that we should recognize the substance as copper. It will perhaps be well to probe this matter a little farther. When we think of a piece of copper we are apt to picture it as distinct from other elements, sodium, zinc, &c., not owing to a difference in the fundamentals out of which it is composed but to the fact that the electrons and so forth are describing, in the atom, more or less definite paths peculiar to the element. Nevertheless, in our mind's eye, we keep the sodium electrons locked up in the sodium, and the copper electrons in the copper. It is, however, possible for us to imagine the various electrons of the copper dissected out and linked together in new configurations so as to form something else, some element of lower atomic weight for example, and even in the general case where we concern ourselves with more general types of coordinates than those associated with the centres of gravity of the electrons, the transition from copper to the other element is capable of being pictured as the mere readjustment of the magnitudes of these more generalized coordinates to the values or range of values appropriate to the second element. It is the same dynamical system which concerns us in each case, however. Even though the operation of transmutation may be impossible by dynamical evolution, the mathematical analysis on which the infinite probability of the state represented by (2), (3), &c. is based will take cognizance of all such arrangements, and indeed of all conceivable arrangements of the coordinates. For all that the mathematics is concerned with is how many coordinates there are: given this, it will make no use of the fact that the substance is copper, for example, but, in estimating the probability, it will include in its survey all the other possible elements, compounds, &c., which can conceivably be produced by dissecting out the

coordinates of the copper and rearranging their magnitudes so as to correspond to other kinds of matter. The mathematics includes in its survey every case in which the values of the coordinates can be conceived as arranged to correspond to states other than those of the elements of matter. Thus for example, if we could take as our coordinates in a piece of matter the ordinary spacial and momental coordinates of the positive and negative electrons, supposing such to exist, the mathematics involved in establishing the infinite probability of the state given by (2), (3), &c., would insist on considering in addition to all those cases corresponding to the various species of matter, all those arrangements in which the positions and velocities of the electrons were distributed in more or less random fashion after the manner of gas molecules.

When we view matters in the above light, it would not seem surprising if the whole of those arrangements which we should be prepared to recognize as copper were associated with only an infinitesimal proportion of the generalized space corresponding to the prescribed energy-range. In fact, is not the infinite probability of the state represented by (2), (3), &c. dependent on the fact that the mathematics takes account of all those distributions of energy among the generalized coordinates which we more particularly associate with the random gas molecule type?

Now in connexion with the above arguments, it might be objected that although at some particular view, all the representative points corresponding to the various copper pieces referred to above might exist in one of the "abnormal" regions of the generalized space, yet, since the abnormal regions form only a small fraction of the total volume of the portion of the space concerned, it will not be long before a point has passed out of the abnormal region into a normal one. It must be pointed out in this connexion, however, that though the abnormal regions corresponding to our piece of copper, for example, may form an infinitesimal fraction of the volume of the available space, they need not be of such a kind that all of the coordinates are constrained to suffer but limited ranges of variation in order to remain within the region. Neither is it necessary to assume that the practical permanence of the copper, as copper, is to be represented by the coordinates all lingering near certain definite values; the abnormal regions may in fact be distributed linearly over great distances in the space like a thin channel permeating hither and thither in a solid block in three-dimensional space. In this

way, the continuity of flow of the representative points from the normal to the abnormal regions of the generalized space may be preserved without the time during which the points remain in the abnormal regions being constrained to be very short, and without there being any congestion of the points such as would be contrary to the Hamiltonian laws as represented by Liouville's theorem of differential invariance. The ideas in this connexion may perhaps be made clearer by a general consideration of the kind of motion which a point must have in the generalized space if it is to correspond to such a system as a piece of copper.

To fix our ideas, let us for a moment suppose that the positions and momenta of the positive and negative electrons are proper generalized coordinates in terms of which to specify the system. In our piece of copper we have a condition of affairs where, viewed from a somewhat crude standpoint, the electrons are all describing comparatively fixed orbits; or perhaps it would be better to say that the average constancy in general feature peculiar to the material as a whole is retained not so much by the orbits remaining fixed as by a condition of affairs in which a change of one kind in one direction in one atom (change of orbital radius, or expulsion of an electron, for example) is on the average balanced by a change of the reverse kind in some other atom. Individual coordinates may be changing continually, and this provides a means by which the point in the generalized space may travel along continuously, and not be confined to the neighbourhood of one spot. If at any instant we fix on the coordinates associated with one atom, find the two-dimensional coordinate planes, in the generalized space, containing the axes of *these* coordinates, and project the motion of the point in the generalized space on these planes, we shall get a certain group of curves. If we do the same thing for the other atoms we shall find that the group of curves is repeated in its general characteristics. This possibility of picking out, from the whole set of coordinate planes of the complete system, groups of coordinate planes such that the projection of the representative point on one group is similar to the projection on other groups, symbolizes the similarity of the atoms.

The permanence of the system is not necessarily symbolized, however, by each of these groups of projections maintaining its form permanently (forming re-entrant paths), for an electron, for example, may leave one atom and become part of another, so that what were formally the coordinates of one atom may in a little while be distributed in a very complex

manner throughout many atoms. This phenomenon would be symbolized by the fact that if we continued to watch the projection of our point on the above set of planes, it would, after a time, begin to lose the regularity of its form in some of the projections. Projections on other coordinate planes not originally associated with the atom in question, and which possibly before showed no definiteness in shape, would, however, begin to acquire such definiteness, of a kind similar to that lost by the projections above mentioned. In this way the practical permanence of the system in its general characteristics would be symbolized, and it will be seen that the maintenance of such permanence of the identity of one kind of material does not require that the representative point for the system shall remain near one spot in the generalized space, or even that it shall trace a re-entrant path. Indeed, there is nothing to prevent the very long (in the generalized sense) path which the point traces as the representative of, say, copper, from ultimately merging into a path corresponding to a normal state*, the slow transition towards this state corresponding physically to a gradual transmutation of the copper to elements of lower atomic weight by radioactive change and so on, down to the condition where all atomic structure was eventually lost, and there remained only chaotic motions of the electrons or other entities, whatever they be, which form the fundamental bricks out of which matter is composed. In case it may be considered that the infinite improbability of any state other than the normal state makes it remarkable that there should be any structure in matter at all, we may remark that this point involves the question of how the matter was created, and we may even go to the length of pointing out that it is only during the comparatively rare period that matter may on the above argument be considered to exist as such, that there will be found those specialized pieces of matter called human beings to study it.

Although in the above remarks radiation has not been specifically mentioned, there is nothing to limit the fundamentals of the arguments to the case where radiation is absent.

Consequences of Equipartition.

The foregoing section forms a criticism of the statement that the "ordinary dynamics" necessitates equipartition of

* This has nothing whatever to do with the question of the slow approach to the normal state as discussed by Jeans (Phil. Mag. vol. x. (1905) p. 91) for the case of radiation.

energy. Even though the theorem itself is admitted, however, considerable care is necessary in its application, and in what follows, without questioning the truth of the theorem, even for ordinary matter, we shall inquire whether some of the difficulties associated with its apparent consequences are not due to its erroneous application.

Equipartition of energy between electrons inside and outside the atoms.

It is frequently stated that the theorem leads to the conclusion that there should be equipartition of energy between the electrons inside the atoms, and the free electrons outside. Admitting for the moment that the ordinary coordinates and momenta of the electrons are suitable generalized coordinates in terms of which to express the system, it is to be noted that the theorem tells us that it is infinitely probable that if we take the average energy of any p coordinates at any instant, the result will be the same as that obtained by taking the average energy of any other group containing say q coordinates, p and q being large numbers. Now it would obviously not be fair, if, before picking out our p coordinates, we asked to be told the energy of each coordinate at the instant and then put only the coordinates of high energy in the p group and only the coordinates of low energy in the q group; yet, when we discuss the relation between the average energy of the electrons inside, and the average energy of the electrons outside, are we not implicitly grouping the coordinates in a manner very largely determined by their magnitudes, or at any rate by relations in which these magnitudes play a fundamental part? Are we not, in fact, grouping them in a manner of which the above example is a crude illustration? It is true that the theorem of equipartition of energy places no restriction on the method of grouping the coordinates, but in whatever way we group the electrons, if for example we place in one group only the electrons which at the particular instant concerned are to be found inside atoms and in the other group only electrons which are to be found outside atoms, we must not be content to merely compare the average energies of the electrons at the instant when we grouped them. We must fix our minds on the identical electrons which we have chosen, and follow them over a very long period of time. During this period, the various electrons which were all inside atoms originally will have opportunities of coming out and re-entering atoms several times, so that for the greater portion of the time the two groups

will lose all distinguishing characteristics, each group having some of its members inside, and some outside atoms. We must, during the long period of time referred to, compare the average energies of the groups again and again *, and all that the theorem of equipartition of energy is capable of telling us (when properly applied) is that, in all but a relatively infinitesimal proportion of such comparisons, the average energies will be equal. The theorem, however, does not deny that the averages may be unequal in certain isolated cases, and such cases are of course artificially brought into prominence when we initially arrange the groups so that one contains only electrons which are inside atoms, and the other contains only electrons which are outside atoms. It is true that the above argument would not apply if the electrons inside atoms always remained inside; such a case, however, would not be one to which the theorem of equipartition would profess to apply, for in this case it becomes denied at the outset that the system can pass through all phases consistent with the conservation of energy †.

Again, if we consider a mixture of two gases, say oxygen and hydrogen, and suppose that there are electrons inside the atoms of each gas, and also free electrons, the theorem of equipartition of energy, even if applicable, would not tell us that we could equate the average energy of the electrons inside the hydrogen molecules to the average energy of the electrons inside the oxygen molecules, or to the average energy of the free electrons. It is only when we consider the average in accordance with the remarks above, or more crudely when we choose two groups each of which has a large number of members drawn more or less indiscriminately from the oxygen, hydrogen, and free electrons that the theorem enables us to equate the averages, and in this case of course the result could be predicted without the theorem, and is indeed a conclusion of no interest. In fact, the theorem in such cases tells us practically nothing at all, and the same difficulty must always present itself when we imagine all the matter concerned as specified by coordinates which are of the same kind. According to the

* Strictly speaking, the instants at which comparisons are made should be so timed that if the corresponding representative points are plotted in the generalized space, their distribution along the stream-line will be the same as it would be in the case of a uniform distribution of points throughout the whole space.

† It must be remarked, however, that violation of this condition does not necessarily invalidate equipartition, since equipartition holds for such a large proportion of the generalized space.

old view of things, in which the coordinates of a hydrogen and of an oxygen molecule were pictured as of different classes, the theorem did really lead to a definite conclusion, viz., that the average energy of the hydrogen molecule was the same as that of the oxygen molecule; for if we imagine the p group of coordinates as drawn from the oxygen molecules and the q group as drawn from the hydrogen molecules, then no matter how long may be the time for which we observe these groups, the p group will always be exclusively oxygen, and the q group will be hydrogen, so that the equality of the averages as predicted by the theorem is, in this case, a result of interest.

Thus, as we have seen above, the absence of equipartition of energy between the electrons inside and outside atoms would not in itself lead to any contradiction with what might be expected from a proper application of the theorem of equipartition. An apparent contradiction, to the application to ordinary matter, of the general theory discussed on pp. 65-67, would arise, however, when we found, as we should find, that at any instant the number of coordinates in the system, having magnitudes between assigned limits, was not given by a formula of the type (2), with p replaced by the total number of coordinates. The failure of the truth of this result would mean that the system was not in the normal state.

Does equipartition of energy require that the energy of a dynamical system with an infinite number of coordinates should be infinite?

The chief field in which the question here referred to becomes involved is that of temperature radiation, where the coordinates of the system are associated with the modes of vibration into which the radiation field can be analysed. It is generally maintained that equipartition does lead to the above conclusion, the argument being somewhat as follows:—“Suppose that a perfect gas forms part of the system. If T is the temperature, and if, further, we write $RT/2$ for the average energy of a degree of freedom of the perfect gas, then equipartition requires that the average energy of any of the other degrees of freedom shall be $RT/2$. Since, in the case of radiation, the number of modes of motion in the æther—and so the number of coordinates—is infinite, and since R can be measured and is found to be finite, the

conclusion is that the total energy of the system must be infinite" *.

Now, quite apart from the question as to whether the theorem of equipartition is justifiable as applied to an infinite number of degrees of freedom, a point which it is not proposed here to discuss, it seems that even in assuming the theorem we ought to be very careful to consider whether the quantity R which figures in the *measurements* on gases is really the R which ought to figure in the expression $RT/2$ for the energy associated with one degree of freedom above concerned. If it were true that the energy were expressible as the sum of squared terms, part of the sum involving the ætherial modes of motion, and part involving the velocity coordinates of the centres of gravity of the molecules, the argument would indeed be justifiable; but nobody would maintain that the interaction between the radiation and the gas was capable of being discussed completely in terms of a sort of interaction between the waves and the centres of gravity of the molecules. If we picture minutely the phenomenon of two gases coming into temperature equilibrium by means of radiation alone, we are constrained to imagine electronic orbits and so forth in the molecule, with the various parts mutually influencing each other. The radiation from the

* The argument is usually developed by considering the case of a box with perfectly reflecting walls inclosing pure æther only. It may be of interest to point out that there is a fundamental difference between the meanings to be attached to a coordinate associated with the ætherial vibrations and such a coordinate as one of the ordinary coordinates of a gas molecule for example. The number of harmonic modes comprised between certain wave-length limits in a box of volume V is half the number comprised between the same wave-length limits in a box of volume $2V$; but the increased number of coordinates in the larger box is not obtained by a *duplication* of the coordinates in the smaller box, as it would be in the cases of two boxes containing ordinary gas molecules, and in which the coordinates concerned were the ordinary coordinates of the gas molecules. It is obtained rather by an interpolation of *extra* wave-lengths which were not capable of existence in the smaller box. The scale of the Fourier analysis is, in fact, more fine-grained in the larger box than in the smaller. These considerations are only of subsidiary importance, however, for the mathematical analysis takes no account of the *nature* of the coordinates. Again, although in the sense above explained, the *quality* of the radiation in the box of volume $2V$ may be said to be mathematically different from that in the box of volume V , that which is observed in any optical instrument, viz. the energy density of the radiation comprised between assigned ranges of wave-length, is the same for each case, the average amplitude of the harmonic modes in the larger box being smaller than the average amplitudes of the smaller number of harmonic modes in the smaller box.

hotter gas increases the motion of the molecules of the cooler gas not by a sort of knocking process directed at the centre of gravity, but by a very complex electromagnetic process involving the structure of the atom. We do not escape the difficulty by defining a perfect gas molecule as one whose actions *are* representable in terms of the positions and motions of its centre of gravity alone; for such a molecule would have its power of interacting with radiation defined out of it. Neither do we escape the difficulty by observing that the energy is *approximately* expressible as the sum of terms corresponding to the motion of the gas molecules alone. Indeed, the matter stands somewhat in the following light:—The whole energy of the system is approximately expressible as the sum of squared terms corresponding to the molecules alone, and we may reasonably expect approximate equipartition between these terms, together with an approximate conformity to the so-called perfect gas laws. Such a specification can, however, tell us nothing about the radiation or its relation to the gas constant; for it is only by the neglect of the radiation that the approximate equipartition results. The energy may, however, be expressible approximately, or possibly exactly, in a much more fine-grained manner as the sum of squared terms, some of which correspond to the modes of ætherial vibrations, and some of which owe their origin in some way to the matter, and are apart from what is ordinarily understood as radiation. When this mode of expression is adopted, it becomes necessary to introduce into the statistical theory determining the partition of energy between the different terms, those restricting relations, whatever they are, which provide for the permanent existence of the molecule as such. It may be that some law other than equipartition will result; but even if equipartition does result, it is not to be anticipated that the average energy of one of the coordinates which correspond to the system as expressed in this fine-grained manner will have any connexion with the average energy of a coordinate of the system when the latter is expressed in the entirely different and approximate manner in terms of the ordinary coordinates and momenta of the molecules. It might be thought that, although for the purposes of the radiation theory it is necessary to represent the molecule in terms of a large number of additional coordinates, yet the average energy of one of these coordinates would be the same as the average energy of the centre of gravity of the molecule itself, just as the average energy of the centres of gravity

of the molecules in a Brownian particle is the same as the average energy of the centres of gravity of the Brownian particles themselves*. Such an analogy would, however, not be in general justifiable; for the truth of the result in the case of the Brownian particles depends in part on the circumstance that the coordinates of the fine-grained specification in terms of molecules are of the same *type* as those which correspond to the Brownian particles themselves.

By eliminating the conception of the molecules as such and going down to the more fine-grained specification in terms of electrons, we introduce more perfect precision into the problem, but we do not avoid the fundamental difficulty discussed above. We have now to deal with a purely electromagnetic problem. The total electromagnetic energy within a cavity bounded by perfectly reflecting walls is

$$(8\pi c^2)^{-1} \iiint (E^2 + H^2) d\tau,$$

where E and H are the electric and magnetic vectors respectively, and c is the velocity of light. It is possible to throw this expression for the energy into a form which represents it approximately as the sum of terms proportional to the squares of the electronic velocities, and of terms corresponding to trains of plane waves in the cavity. When the electrons are absent, and only the plane waves are present, it is possible to express the energy exactly as the sum of squares, and, moreover, to show that the equations which govern the waves can be thrown into the Hamiltonian form. When free electrons are present, however, *their* equations of motion do not conform to the

* It will be recalled that if the energy of a system of particles be expressed as the sum of squares of quantities proportional to the ordinary three-dimensional coordinates and momenta of the individual particles, then if, in our mind's eye, we separate out any group of particles and choose the coordinates anew, so that six of them correspond to the ordinary three-dimensional coordinates and momenta of the centre of gravity of the group, the energy will still take the form of a sum of squares for the new choice of coordinates. Further, the Hamiltonian equations will apply to the new specification if they applied to the old one, so that equipartition of energy will result between the energies of the centres of gravity of such groups, and it will also result between these energies, and the energies of the individual molecules which have not been mentally collected into groups, and, by a slight extension of the argument, it may be seen to result between the energies of the centres of gravity of the groups and the individual molecules which compose the groups. It is not even necessary, for the application of the argument, that the groups shall consist of particles which are all in a cluster; some of the members of a single group may be miles apart, and several groups may overlap.

Hamiltonian type. Apart from the objection which this fact alone throws in the way of our equating the energy of the electron to the average energy of the ætherial vibrations, however, there exists the other difficulty that when the coordinates are chosen so that some of them are the ordinary coordinates and momenta of the electrons, the energy is not *exactly* expressible as the sum of squares, or even of terms each of which depends upon only one of the coordinates chosen.

It may be thought that, in so far as the energy is approximately so expressible, equipartition should result between the energies of the electrons and those of the ætherial vibrations, at any rate as an approximation. Such an expectation is not justifiable, however; for suppose that, in order to obtain an exact specification, it were necessary to represent what is called the energy of the electron as the sum of an infinite number of terms, in a manner analogous to that in which the radiation energy is expressed in the absence of electrons. Then, if the dynamical laws applicable to this specification, and the restricting conditions which provide for the permanent existence of the electrons, permitted a state of equipartition at all, it would be the average energy of these terms, which together make up the energy of the electrons, which would have to be equated to the average energy of the ætherial vibrations. The former quantity would, in general, form only an infinitesimal fraction of the whole energy of the electron. To put the matter rather crudely, we are frequently accustomed to imagine that the state of the electron is completely specified when its velocity is specified, but, in the more fine-grained analysis, the mathematics is able to see an infinite number of different arrangements of field which correspond to a given velocity: it is not endowed with the "common sense" which would enable it to see that for a variety of purposes the electron acts in the same general sort of way for all of these slightly varying conditions, and in estimating the probability of a given state, it is bound to take cognizance of all these possible variations.

As we have already remarked, and as is in fact well known, the field in a cavity containing no electrons can be expressed in a series of "normal functions" (in this case, sine and cosine functions), and the fundamental coordinates which specify it in this form obey the Hamiltonian equations. It would be interesting if, in a cavity, we could express the complete field, including the field of the electrons, as a series of normal functions, so that the total energy

$$(8\pi c^2)^{-1} \iiint (E^2 + H^2) d\tau$$

could be expressed as the sum of terms depending on the individual coordinates peculiar to the normal functions. The application of statistical reasoning to the problem, subject to the constancy of the total energy, and to the restricting conditions which provide for the permanence of the electrons, would then lead to the law of partition of energy between the individual terms in the expression for the energy, provided that, by means of the electromagnetic equations, the laws governing the changes of the coordinates could be thrown into the Hamiltonian form. This is, of course, only a rather more precise method of formulating the problem outlined above, but it serves to show how, in an exact specification of this kind, the electron, as such, would disappear from the analysis, its sole representative being the restricting conditions which provide for the permanence of its existence.

In spite of all that has been written above concerning the objections to connecting the gas constant R with the radiation formula through the medium of arguments such as those which have been here reviewed, there remains the remarkable fact that the R which occurs in the equipartitional formula,

$$E_{\lambda} = 8\pi RT/\lambda^4,$$

a formula true for long wave-lengths, is found to be actually equal to the gas constant experimentally obtained in other ways. The difficulty presents itself as to how it is that, if the arguments accounting for the presence of R in the radiation formula are wrong, as they appear to be, they nevertheless do predict the presence of the correct constant.

The analogous difficulty is not avoided in the arguments which purport to explain the presence of the gas constant in the more exact formula of Planck; and although it would appear impossible to import complete precision into the problem without a knowledge of the mode of interaction between the molecules and the radiation, the following tentative considerations may nevertheless be of interest.

Relation between the radiation formula and the average energy of a gas molecule.

Suppose that although we may not know the reasons underlying the radiation formula, we nevertheless know that the value of E_{λ} is determined as a function of λ and of the temperature T by the formula

$$E_{\lambda} = \frac{8\pi}{\lambda^4} \frac{h\nu}{e^{h\nu/kT} - 1}, \quad (4)$$

where no other significance is attached to h and k other than that they are constants. k is at present in no way associated with a gas molecule, and, indeed, we shall not attach any significance to T other than that it represents the quantity which we measure as the temperature. Let us in fact for the moment look upon (4) as a mere empirical relation. Let us now suppose as a very special case that there are some perfectly free electrons in the radiation field. Although we may not know the equations of motion exactly, yet we know them with a sufficient degree of approximation to be able to ascertain with some accuracy how the electron will behave in the field. Planck has shown that an oscillator of frequency ν , when placed in a radiation field, will take up an average energy U where $E_\lambda = 8\pi U/\lambda^4$. Hence, twice the average value of the kinetic energy assumed by a resonator of frequency ν , when placed in a radiation field, will be

$$U = \frac{\lambda^4}{8\pi} E_\lambda = \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1}.$$

For $\nu=0$ we obtain the case of a free electron, and *

$$U_{\nu=0} = L t_{\nu=0} \frac{\lambda^4 E_\lambda}{8\pi} = kT.$$

Thus, quite apart from any theory as to the origin of the formula (4) and as to the meaning of k and T , if only we know that (4) is correct, we can say that twice the average energy per degree of freedom of an electron placed in the field will be kT . We have, in discussing this matter, so far used kT instead of RT in order to enforce the idea that we are not looking upon the kT occurring in (4) as fundamentally equal to twice the energy of a degree of freedom of a gas molecule, but for the sake of uniformity we may now replace k by R , and we may then note that on the above view we are not adopting the attitude that the quantity RT occurs in the radiation formula because $RT/2$ is the average energy of one component of the motion of the free electron in the field, but rather are we adopting the view that the electron moves with

* This step is not quite rigorous, for although it appears generally to be assumed (see Jeans, "Report on Radiation and the Quantum Theory," p. 14) that a free electron may be treated as an oscillator of zero frequency, the nature of the mathematical reasoning does not appear to warrant this assumption rigorously. It is proposed to enter into this matter more fully in a later communication; but as the practical conclusions are not materially affected, it is not intended at present to complicate the considerations by going more deeply into this matter.

the average energy $RT/2$ per degree of freedom, because this is the quantity which is contained in the appropriate place in the radiation formula. The direct extension of this argument to the case of a gas molecule is not so easy, because we do not know the mechanism by which the molecule is set in motion by the field. Suppose, however, that it is justifiable to extend the result to gas molecules, a step to which we are encouraged by the fact that other considerations lead to equality of the average energy of gas molecules and free electrons; suppose, in fact, that it is true that in the general case the laws by which the molecules are set in translatory motion are such that

Twice average energy of gas molecule at temp. T

$$= Lt_{\nu=0} \frac{\lambda^4 E_{\lambda}^*}{8\pi}, \quad \dots \quad (5)$$

then, if we take Planck's formula for E_{λ} , we have, as before, that the fundamental origin of the quantity R is in the radiation formula and not in the gas molecule, and that it is on account of the occurrence of the quantity RT in the radiation formula that the molecule moves so that the average energy of a translatory degree of freedom is $RT/2$. A view of this kind is all the more reasonable when we realize that it is only ultimately through the radiation that two gases, for example, which are separated from each other, can come into temperature equilibrium. Even conduction, when viewed from a fundamental standpoint, probably partakes more nearly of the nature of radiation than of what is ordinarily implied in the term conduction.

It is of interest to generalize the above arguments in the following form:—

Suppose that it be known empirically, or by some theoretical argument, that E_{λ} is of the form

$$E_{\lambda} = \frac{8\pi}{\lambda^4} \cdot \frac{av}{e^{af(T)} - 1},$$

where a is a constant, and $f(T)$ is some function of the temperature of which we do not yet know the form. Let us even go so far as to say that we have not yet decided how temperature is to be measured. If we follow the line of the arguments above, and assume the relation

$$U_{\nu=0} = Lt_{\nu=0} \lambda^4 E_{\lambda} / 8\pi,$$

* Strictly speaking, the average concerned in (5) is a time average for a single coordinate, while the average concerned in equipartition is an average taken over a number of coordinates at a constant time. The difficulty in this respect is not, however, of fundamental importance, and we shall not dwell further upon it.

we find that, if an electron, or (by an extension of the argument) a gas molecule, is placed in the radiation field, twice the average energy assumed by a translatory degree of freedom of such an electron or molecule will be

$$U_{\nu=0} = \left[\frac{a\nu}{e^{\nu f(T)} - 1} \right]_{\nu=0} = \frac{a}{f(T)} \cdot \cdot \cdot \cdot \cdot \quad (6)$$

Now, if we decide to measure temperature as a quantity proportional to the average energy of a degree of freedom of a gas molecule, then, in view of (6), this fact alone determines $f(T)$ to be proportional to $1/T$; and if further we choose the size of our temperature degree in the usual way, *i. e.* in a way which makes $U_{\nu=0} = RT$, we see that $a/f(T)$ becomes determined as equal to RT . Thus, again, the origin of the quantity RT is in the radiation formula. This formula determines twice the average energy of a degree of freedom of the molecule to be $a/f(T)$, and because we measure temperature in the way we do, this is equal to RT^* .

According to the usual theories the relation between the gas molecule and the radiation formula is traced through the law expressing the entropy of the system in terms of the probability; and on this line of argument, the necessity for imagining some form of quantum theory for the radiation appears essential. Developments of the radiation formula not involving this finite quantum concept have been attempted, principally by Larmor; but though it would appear, from the arguments of Larmor, that the necessity for the finite quantum can really be avoided, there appears to be difficulty in making the theory predict the numerical equality between the constant R in the radiation formula and the gas constant. The view tentatively suggested above as to the connexion between the two, is somewhat fruitful in filling in the gap, and it also has a bearing on Poincaré's treatment of the problem of radiation, according to which it was claimed as proved that a quantum theory was necessitated by the mere fact of the energy per c. c. of a body being finite and not infinite. It is proposed to discuss these matters in a subsequent communication.

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* It must of course be remarked that the above view does not contain as an obvious consequence the Maxwellian law of velocity distribution among the molecules. It would take us too far afield to attempt to inquire into this matter in detail.

VI. *Some simple Deformations of Homogeneous Partitionings of Space and the Increase of Internal Surface generated thereby.* By EMIL HATSCHKE *.

THE investigation to be described here was originally undertaken with the object of determining whether the generally received theory of the structure of gels (jellies) was compatible with the elastic properties of these bodies. This theory assumes that gels are systems of two liquid phases having interfacial tension.

Since a number of gels show marked, and within narrow limits perfect, elasticity of form, it follows at once that, if the theory is correct, this elasticity can be due only to the interfacial tension of the phases, since either phase considered singly possesses elasticity of volume only. Deformation of a gel must lead to an increase of the interface or internal surface, and the tendency of the system to return to its minimum interface shows itself as elasticity. We can, therefore, without at present making any assumptions as to the geometric character of the interface, at once say that—for, say, a tensile strain W and elongation L —

$$WdL = CdS \quad \text{or} \quad W = C \frac{dS}{dL},$$

where S is the interface and C a constant containing both its absolute size and the interfacial tension. If, therefore, we can determine the function connecting elongation and increase of surface, we can find the stress-elongation curve by differentiation and can compare the curve so found with experimental data. If the curves show marked disagreement the theory of two liquid phases is at once untenable.

As regards the shape of the interface, we have, of course, to make assumptions, which, however, are very strictly defined. If a system of two liquid phases is to have approximately the appearance and some of the properties of a solid, we know from the behaviour of emulsions made by Pickering and others that the disperse phase must occupy almost the total volume—98–99 per cent.,—leaving only 1–2 per cent. for the continuous phase, which therefore can form only a thin film separating polyhedra of the continuous phase. Although such a structure can hardly be in stable equilibrium, it can be shown by microscopic examination

* Communicated by Dr. L. Silberstein.

to exist in the high percentage emulsions, and is known to persist for years. This is, no doubt, due to the very low interfacial tension, which is a necessary condition for the production of such emulsions; as gels *ex hypothesi* consist of two phases differing only in concentration, but not in composition, the interfacial tension is likely to be lower even than that between the soap solutions and mineral oils of Pickering's emulsions, so that the continued existence of a polyhedral structure offers no difficulty.

As regards the geometrical character of the interface, we shall hardly be mistaken in assuming that it conforms to some type of homogeneous partitioning of space, and that its elements are either twelve- or fourteen-faced polyhedra. If we determine the increase of surface produced by deforming such a structure and plot the first differential coefficients of these increases as ordinates against the elongations, we obtain, as already explained, the stress-elongation curves. As the physical results of the investigation have been published in a short paper*, it is only necessary to state here that these theoretical curves show very marked disagreement with the experimental stress-elongation curves.

To extend the geometrical investigation to all cases, we shall consider, in addition to dodecahedral and tetrakaidcahedral partitionings, the hexahedral partitioning. If we confine ourselves to polyhedra with straight edges and plane faces, the minimum case, *i. e.* the polyhedron with the minimum surface, will be: for the hexahedral partitioning the cube, for the dodecahedral type the regular rhombododecahedron and for the tetrakaidcahedral type the equilateral cubo-octahedron. As regards the deformation, we are only limited by the condition of continuity that the polyhedra obtained from the minimum types must again fill space continuously. This condition is, of course, satisfied by the following types of deformation, which we will consider in detail:—

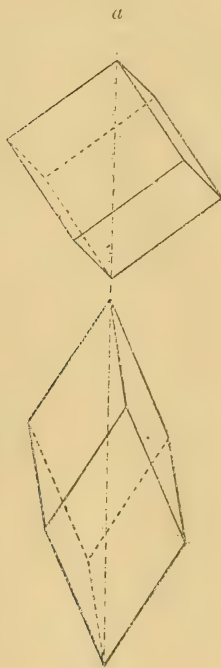
(1) *Hexahedral partitioning*.—(a) The cube is deformed by a stress parallel to four of its edges and transformed into a square prism having the same volume. Although this case appears highly special, it will be found to be in complete functional agreement with all the others.

(b) The cube is deformed by a stress acting in the direction of its space diagonal and all edges remain equal, so that it is transformed into a rhombohedron (fig. 1, *a* & *b*).

* Trans. Faraday Society, vol. xii. pt. 1 (1916).

Dodecahedral partitioning.—(a) The regular rhombo-dodecahedron is deformed by a stress acting in the direction of its crystallographic axis, *i. e.* the axis passing through two opposite four-faced corners. In this position it may be

Fig. 1.

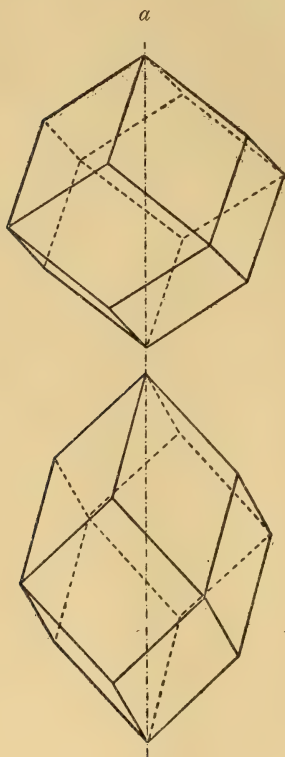


looked upon as a combination of the tetragonal pyramid with the tetragonal prism of the other order, and the deformed polyhedron retains this general character. We assume that all edges remain equal, so that the deformed polyhedron will be bounded by rhombs of two kinds, eight belonging to the pyramid and four to the prism (fig. 2, *a* & *b*).

(*b*) The regular rhombo-dodecahedron is deformed by a stress acting in the direction of the axis passing through two opposite three-faced corners. In this position it may be looked upon as a combination of the hexagonal prism with a rhombohedron, and the deformed polyhedron retains this

general character. We assume that all edges remain equal, so that the deformed polyhedron will be bounded by rhombs

Fig. 2.

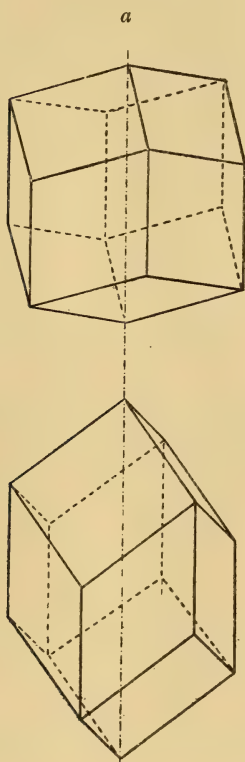


of two kinds, six belonging to the prism and six to the rhombohedron (fig. 3, *a* & *b*).

Tetrakaidecahedral partitioning.—The equilateral cubo-octahedron is deformed by a stress acting in one of the axes of the octahedron. The polyhedron may be looked upon as a combination of a tetragonal pyramid with the pinakoid and the prism of the opposite order, and preserves this general character when deformed. To ensure continuity the following conditions must, however, be satisfied: the eight regular hexagons are transformed into symmetrical hexagons, having two pairs of sides all equal to one-third of the polar edge of

the pyramid and one pair of sides equal to one-third of the basal edge of the pyramid ; the two pinakoid faces remain

Fig. 3.

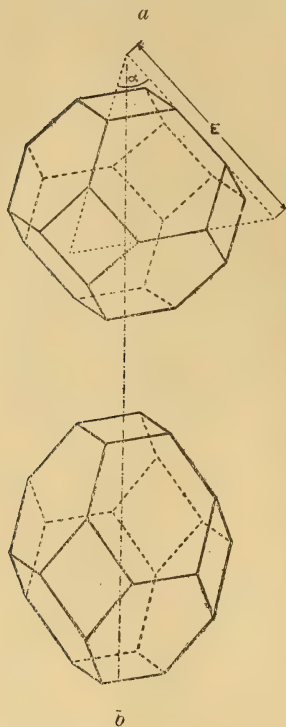


squares, and the four prism faces become rhombs (fig. 4, *a* & *b*).

As stated explicitly under (1) *a*, the volume is supposed to remain constant in all cases, this condition arising from the original problem, in which two liquid phases were considered. As the calculation for the cube transformed into a square prism is extremely simple, we will consider it before describing the method adopted in the other cases.

If a cube of unit edge and unit volume is transformed into a square prism of the height *L* and the same volume, the

Fig. 4.



surface of this prism will be

$$S = \frac{2}{L} + 4\sqrt{L}$$

and the increase in surface for the elongation $L-1$ will be

$$S - S_m = \frac{2}{L} + 4\sqrt{L} - 6,$$

S_m being the surface of the minimum polyhedron, *i. e.* the cube.

The curve defined by this equation is plotted in fig. 5, with L as abscissæ and $\frac{S - S_m}{S_m}$ as ordinates. For $L < 1$, *i. e.* for compression, the ordinate grows rapidly and becomes ∞ for $L=0$. For $L > 1$ the curve has a marked inflexion, and the value of the abscissa at which the inflexion occurs is found by two successive differentiations to be $L = \sqrt[3]{16} = 2.5198$, or an elongation of 152 per cent. This curve is marked "P" for $L \geq 1$.

As regards the deformations under (2), (3), and (4) it is immediately obvious that, with the assumptions we have made, it is possible to express the volume and surface of each polyhedron as a function of the length of the edge and at any one angle in any of the rhombs, preferably the angle of the pole α . For the cubo-octahedron it is most convenient to refer the calculation to the whole edge of the pyramid and the angle at the apex of the latter (fig. 4, *a*). As the volume is to remain constant, we have to find the volume of the minimum polyhedron, for which the value of α is known, taking the edge as being of unit length, and have then to calculate the edge E for various values of α , so that the volume is the same as that of the minimum polyhedron with the edge of unit length. The other quantities of interest to us can then be expressed in terms of E and α ; they are the total surface and the length of the axis (for the cubo-octahedron the distance between the square faces). The expressions found are as follows:—

I. Cube stretched along space diagonal and transformed into rhombohedron. (Fig. 1, *a* & *b*.)

$$E = \frac{1}{\sqrt[3]{2 \sin^2 \frac{\alpha}{2}} \sqrt{3 - 4 \sin^2 \frac{\alpha}{2}}}. \quad L = 3E \sqrt{1 - \frac{4}{3} \sin^2 \frac{\alpha}{2}}.$$

$$S = 6E^2 \sin \alpha.$$

II. Rhombo-dodecahedron stretched along crystallographic axis. (Fig. 2, *a* & *b*.)

$$E = \frac{1}{\sqrt[6]{27 \cos \alpha \sin^4 \frac{\alpha}{2}}}. \quad L = 4E \sqrt{\cos \alpha}.$$

$$S = 8E^2 \left(\sin \alpha + \sin \frac{\alpha}{2} \sqrt{2 \cos \alpha} \right).$$

III. Rhombo-dodecahedron stretched along axis passing through two opposite 3-faced corners. (Fig. 3, *a* & *b*.)

$$E = \frac{2}{\sqrt[3]{9 \sin^2 \frac{\alpha}{2} \left(1 + \sqrt{1 - \frac{4}{3} \sin^2 \frac{\alpha}{2}} \right)}}.$$

$$L = E \left(1 + 3 \sqrt{1 - \frac{4}{3} \sin^2 \frac{\alpha}{2}} \right).$$

$$S = 2E^2 \left(3 \sin \alpha + \sqrt{12} \sin \frac{\alpha}{2} \right).$$

IV. Cubo-octahedron stretched along axis of octahedron.
(Fig. 4, *a* & *b*.)

$$E = \frac{1}{\sqrt[3]{4 \sin^2 \frac{\alpha}{2} \sqrt{2 \cos \alpha}}} \quad L = \frac{4}{3} E \sqrt{\cos \alpha}.$$

$$S = \frac{8}{9} E^2 \left(3 \sin \alpha + \sin^2 \frac{\alpha}{2} + \sin \frac{\alpha}{2} \sqrt{2 \cos \alpha} \right).$$

(N.B.—For this polyhedron E =the whole edge of the square pyramid, α the angle at the apex of the latter, and L the distance between the two square faces.)

A number of values have been calculated, for elongation only, from these formulæ, and are given in the table below :—

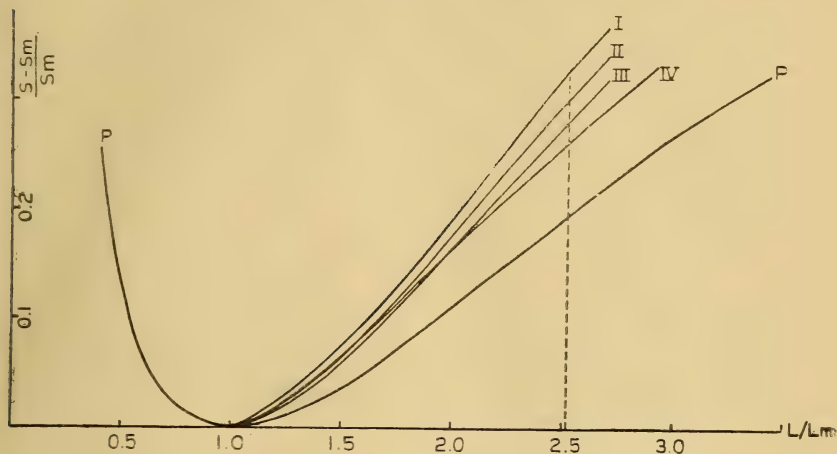
| | | E. | L. | S. | $\frac{L}{L_m}$ | $\frac{S-S_m}{S_m}$ |
|------|--------------|-------|-------|--------|-----------------|---------------------|
| I. | 90° | 1.000 | 1.732 | 6.000 | 1.000 | 0.000 |
| | 75 | 1.031 | 2.194 | 6.158 | 1.267 | 0.026 |
| | 60 | 1.112 | 2.745 | 6.545 | 1.585 | 0.091 |
| | 45 | 1.300 | 3.499 | 7.171 | 2.020 | 0.195 |
| | 30 | 1.653 | 4.732 | 8.193 | 2.732 | 0.366 |
| II. | 70° 31' 44" | 1.000 | 2.304 | 11.313 | 1.000 | 0.000 |
| | 60° | 1.029 | 2.906 | 11.564 | 1.261 | 0.022 |
| | 50 | 1.094 | 3.526 | 12.037 | 1.530 | 0.063 |
| | 40 | 1.234 | 4.321 | 12.989 | 1.876 | 0.149 |
| | 30 | 1.456 | 5.420 | 14.258 | 2.352 | 0.260 |
| | 25 | 1.628 | 6.198 | 15.140 | 2.695 | 0.339 |
| III. | 108° 88' 16" | 1.000 | 2.000 | 11.313 | 1.000 | 0.000 |
| | 100° | 1.012 | 2.417 | 11.479 | 1.208 | 0.018 |
| | 90 | 1.041 | 2.843 | 11.803 | 1.422 | 0.043 |
| | 60 | 1.251 | 4.314 | 13.553 | 2.157 | 0.198 |
| | 45 | 1.473 | 5.439 | 14.960 | 2.719 | 0.322 |
| IV. | 60° | 1.000 | 0.943 | 2.976 | 1.000 | 0.000 |
| | 50 | 1.073 | 1.147 | 3.024 | 1.215 | 0.016 |
| | 40 | 1.200 | 1.400 | 3.158 | 1.485 | 0.061 |
| | 30 | 1.419 | 1.761 | 3.398 | 1.869 | 0.142 |
| | 20 | 1.822 | 2.355 | 3.735 | 2.497 | 0.255 |
| | 15 | 2.194 | 2.875 | 4.105 | 3.049 | 0.379 |

The values of $\frac{S-S_m}{S_m}$ have been plotted in fig. 5 as

ordinates against the values of L/L_m as abscissæ. Differentiation of the expressions obtained for these two variables leads, of course, to entirely unmanageable equations, but it is sufficiently obvious that the function connecting elongation and increase is the same in all cases, and therefore of the same type as the comparatively simple function found in

the case of the cube elongated parallel to four of its edges and transformed into a square prism. The inflexion characteristic for this curve is equally apparent in the four

Fig. 5.



others, and occurs, so far as can be judged, at the same abscissa. What the geometrical meaning of this value may be is difficult to see in view of the difference in type between the various polyhedra which have been considered.

The problem which gave rise to the present investigation is probably the first one in which deformations of homogeneous partitionings of space had to be taken into consideration, while the well-known applications of the theory, as made by Osborne Reynolds, Pope and Barlow, and others, did not call for an examination of the changes produced in the partitioning by stresses. Such an examination cannot, however, be avoided in those instances in which a polyhedral structure and the existence of an inter-polyhedral layer with special properties are postulated to account for the peculiarities of systems under stress, *e. g.* the theory of an intercrystalline cement as an important factor in the tensile strength of metals, &c. The results here given, which notwithstanding the somewhat special assumptions seem to point to a uniform behaviour of homogeneous partitionings, may therefore be useful as providing a direct criterion of the validity of speculations which postulate such structures.

VII. *Molecular Refractivity and Atomic Interaction.* By
L. SILBERSTEIN, Ph.D., Lecturer at the University of
Rome, Scientific Adviser to Adam Hilger, Ltd.*

1. *The Additive Law and its Limitations.*

THE modern chemist makes an extensive use of Lorentz's additive law of optical refractivities, especially in the vast domain of organic compounds.

Let μ be the refractive index, M the molecular weight, and d the density of a chemical compound, whose molecule consists of c_1 atoms A_1 , c_2 atoms A_2 , and so on. Let us write

$$N = \frac{\mu^2 - 1}{\mu^2 + 2} \cdot \frac{M}{d} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

for what will be called *the molecular refractivity* † of the compound in question. Then the additive law states that it is possible to ascribe to each of the constituent atoms A_i a certain number N_i (a function of frequency only) called its *atomic refractivity*, such that

$$N = c_1 N_1 + c_2 N_2 + c_3 N_3 + \dots, \quad . \quad . \quad . \quad . \quad (2)$$

no matter what the state of aggregation or the remaining physical conditions of the compound. And it is certainly a very remarkable fact that this additive formula holds, at least within a few units of the second decimal place, in many cases.

If all the ingredients A_i were available as monoatomic substances, accessible to the refractometer, then each N_i could be measured directly. M_i and d_i being the corresponding values of atomic weight and of density, we should have

$$N_i = \frac{\mu_i^2 - 1}{\mu_i^2 + 2} \cdot \frac{M_i}{d_i}.$$

But such is by no means the case. On the contrary, none of the atomic refractivities N_i , contained in the chemist's table, has been obtained directly. The chemist's actual method of procuring atomic refractivities amounts to the following mathematical procedure:—If κ molecular refractivities N of κ different compounds of κ elements are

* Communicated by the Author.

† Some authors call it "the molecular refraction," others "the refraction equivalent" and "molecular refractive power." The above name has seemed more convenient.

experimentally known, as well as the numbers c_1, c_2 , etc. for each of them, then we have κ linear equations of the form (2) and, these being mutually independent, the required κ atomic refractivities are found by solving the system of equations. There is, of course, not the least objection to such a procedure. The question then is whether the values of $N_1, N_2, \dots, N_\kappa$, thus obtained, are consistent with the observed refractivities of other compounds of the same elements. And, as has already been mentioned, the additive law stands this test in a remarkably large number of cases. The chemists, it is true, complain but too often of "exceptions to the rule," and these, especially since J. W. Brühl's time, make up a rather formidable list. To the physicist's mind, however, the surprising fact is that the additive law *does* hold at all in certain cases. For to him it means absence of atomic interaction*, a state of things which one would hardly expect.

At any rate, the chief object of the present paper is to lay stress precisely on what are usually called the "exceptions" and to attempt to derive from these some knowledge about the electrical interaction of the atoms of a molecule.

Before entering upon our subject, it will be well to quote a few numbers exhibiting the degree of approximation with which the additive law holds, and the values of certain extra-terms to be added when the law does not hold. Since the atomic refractivities, as sanctioned by the chemical authorities, do not seem to be easily accessible, it may be advisable to reproduce here, for the sake of reference, the numbers given in Landolt-Börnstein's *Tafeln* (1912), p. 1039, the sources quoted by them in this connexion being: Eisenlohr, *Z. phys. Ch.* (1910), 75, 585, and Roth and Eisenlohr, *Refraktometr. Hilfsbuch*, Leipzig, 1911. The figures given in this Table under the heads $H_\alpha, H_\beta, H_\gamma, D$ are the atomic refractivities N_i for the hydrogen lines α, β, γ of the Balmer series and for the "D-line" of sodium; the last two columns contain the corresponding dispersions of N_i , shortly called the atomic dispersions. The Table contains also the molecular refractivity of the important group CH_2 , and some extra-terms, such as due to a double bond in the case of carbon. In using this Table, and comparing the calculated

* The reader will remember that, in Lorentz's electromagnetic theory of dispersion, the additive law is a consequence of the express assumption that the (dispersive) electric particle contained in one atom is not disturbed by what is going on in the remaining atoms of the same or of other molecules. H. A. Lorentz, *Arch. néerl.* xxv. (1892), p. 363; more recently treated in Lorentz's 'Theory of Electrons,' Leipzig (1909), Chap. IV.

molecular refractivities with the observed ones, we have to remember that the atomic weights are those more recently adopted, viz., 16 for oxygen, 1.008 for H, and so on.

| | Symbol. | H _α . | D. | H _β . | H _γ . | H _β -H _α . | H _γ -H _α . |
|-------------------------------|-----------------------------------|------------------|--------|------------------|------------------|----------------------------------|----------------------------------|
| Group CH ₂ | CH ₂ | 4.598 | 4.618 | 4.668 | 4.710 | .071 | .113 |
| Carbon | C | 2.413 | 2.418 | 2.438 | 2.466 | .025 | .056 |
| Hydrogen | H | 1.092 | 1.100 | 1.115 | 1.122 | .023 | .029 |
| hydroxyl-Oxygen | O' | 1.522 | 1.525 | 1.531 | 1.541 | .006 | .015 |
| ether-Oxygen | O< | 1.639 | 1.643 | 1.649 | 1.662 | .012 | .019 |
| carbonyl-Oxygen | O'' | 2.189 | 2.211 | 2.247 | 2.267 | .057 | .078 |
| Chlorine | Cl | 5.933 | 5.967 | 6.043 | 6.101 | .107 | .168 |
| Bromine | Br | 8.803 | 8.865 | 8.999 | 9.152 | .211 | .340 |
| Iodine | I | 13.757 | 13.900 | 14.224 | 14.521 | .482 | .775 |
| Ethylene bond [double] | = | 1.686 | 1.733 | 1.824 | 1.893 | .138 | .200 |
| Acetylene bond [triple] | ≡ | 2.328 | 2.398 | 2.506 | 2.538 | .139 | .171 |
| Nitrogen in primary amines .. | H ₂ N-c | 2.309 | 2.322 | 2.368 | 2.397 | .059 | .086 |
| „ in secondary amines .. | H ₂ N-(c) ₂ | 2.478 | 2.502 | 2.561 | 2.605 | .086 | .119 |
| „ in tertiary amines .. | N-(c) ₃ | 2.808 | 2.840 | 2.940 | 3.000 | .133 | .186 |
| „ in imides (tert.) ... | c-N=c | 3.740 | 3.776 | 3.877 | 3.962 | .139 | .220 |
| „ in nitriles | N≡c | 3.102 | 3.118 | 3.155 | 3.173 | .052 | .060 |

Let us now test the above figures, whatever their origin, on some concrete examples, retaining in the final results but two decimal figures.

Water.

| | (H _α). | (H _γ). |
|----------------------|--------------------|--------------------|
| 2H | 2.18 ₄ | 2.24 ₄ |
| O' | 1.52 ₂ | 1.54 ₁ |
| <hr/> | | |
| N _{calc.} = | 3.71 | 3.78 ₅ |
| N _{obs.} = | 3.69 | 3.78 |

This can be looked upon as a very good agreement.

Chloroform.

| | (H _α). | (H _γ). |
|----------------------|--------------------|--------------------|
| C | 2.41 ₃ | 2.46 ₆ |
| H | 1.09 ₂ | 1.12 ₂ |
| 3Cl | 17.79 ₉ | 18.30 ₃ |
| <hr/> | | |
| N _{calc.} = | 21.30 | 21.89 |
| N _{obs.} = | 21.31 | |

This again speaks in favour of pure additivity. Notice that thus far we have had no extra-terms. The case is different

with the following examples, in which such terms do play an essential part.

Benzene. Here we have, according to the usual ring-shaped formula, three double bonds between the carbon atoms. Thus,

| | (H _α). | (H _γ). |
|--------------------|--------------------|--------------------|
| 6H | 6.55 ₂ | 6.73 ₂ |
| 6C | 14.47 ₈ | 14.79 ₆ |
| 3 = | 5.05 ₈ | 5.67 ₉ |
| <hr/> | | |
| $N_{\text{calc.}}$ | = 26.09 | 27.21 |
| $N_{\text{obs.}}$ | = 26.0 | 27.1 |

This again is a satisfactory agreement from the point of view of the above Table. However, the mere presence, in the account, of three double-bond terms |= (which gives an item nearly equal to that due to five hydrogen atoms) is a manifest confession of *non-additivity*, *i.e.* of the presence of considerable atomic interaction. Still, in cases like this the chemist does not speak yet of “exaltation” proper. Nor does he call the triple-bond term ≡ an exaltation, the latter name being reserved for such cases in which there are extra’s even to these sanctioned and fixed extra-terms. The discovery of |= is due to J. W. Brühl, who has done much valuable work in this domain*. Notice that |= is as much as $\frac{2}{3}$ of the C-refractivity itself, and, what deserves a peculiar emphasis, the dispersion of |=, from H_α to H_β, is even about six times stronger than that of the C itself. This is equally true of ≡. Yet both of these are looked upon as normal extra-terms, since they are of commonest occurrence. The name of “exaltation,” or, its negative, “depression,” is used when these ordinary extra-terms are insufficient to maintain the additive law, *e.g.* when owing, say, to the proximity or not of two multiple bonds, there is still an outstanding disagreement from that law. But from the physical point of view these extra-terms, primary or secondary, being so many manifestations of non-additivity, will appropriately in all cases be called *exaltations* when positive, and *depressions* when negative, with respect to certain standards. In doing so, however, we must not deprive the double- and the triple-bond terms of their

* The reader may consult Brühl’s account in “The Development of Spectro-Chemistry,” Proc. Roy. Inst. xviii. 1 (1906), p. 122.

special importance. Whatever the nomenclature, the approximate constancy of these extra-terms in a multitude of cases remains a very characteristic feature.

Our above remarks apply equally to the following examples, for which it will be enough to quote the final results only. These examples are taken from Auwers and Eisenlohr's paper, *Berl. Chem. Berichte*, xliii. 813. The molecular refractivities N , calculated and observed, are for the D-line, and the dispersions Σ are from H_a to H_γ :—

Trimethylstyrol [$C_6H_5 \cdot C(CH_3) : C(CH_3)_2$].

$$N_{\text{calc.}} = 49.05 \qquad \Sigma_{\text{calc.}} = 1.85$$

$$N_{\text{obs.}} = 49.55 \qquad \Sigma_{\text{obs.}} = 2.23$$

$$\text{"exaltation"} + 0.50 \qquad + 0.38 = 21 \text{ per cent.}$$

α -Methylstyrol [$C_6H_5 \cdot C(CH_3) : CH_2$].

$$39.85 \qquad 1.63$$

$$40.49 \qquad 2.11$$

$$+ 0.64 \qquad + 0.48 = 29 \text{ per cent.}$$

Styrol [$C_6H_5 \cdot CH : CH_2$].

$$35.24 \qquad 1.53$$

$$36.34 \qquad 2.14$$

$$+ 1.10 \qquad + 0.61 = 40 \text{ per cent.}$$

From these examples we see that, while the "exaltation" of molecular refractivity is comparatively small, the "exaltation" of *dispersion* is very large, amounting in the last example to 40 per cent., and Auwers and Eisenlohr (*loc. cit.*) quote cases in which it becomes enormous, 107 per cent., 153 per cent., and even 277 per cent. Whole classes of cases in which there is a considerable "depression" will be found in Brühl's papers, *Berl. Chem. Ber.* xl. (1907), pp. 878, 900, 1159 *et seq.* The ever growing hierarchy of rules indicating how to treat the exceptions to the law of additivity, although undoubtedly helpful to the chemist, is the clearest confession of non-additivity.

Again, quite apart from the numerical magnitude of disagreement, there are, so to say, qualitative objections to the additive law, which seem very striking, and which, as far as I know, have been entirely overlooked. Thus,

there are *crystalline* compounds, having two or even three different principal refractivities, and (although the regular arrangement of molecules is an indispensable factor) the optical anisotropy of a crystal is certainly to be attributed in its essence to the anisotropy of the molecule. Now, the constituent atoms, or rather their refractivities, as the C or O' or even $\bar{=}$ of the above Table, being essentially isotropic, an additive combination of these is utterly impotent to give an optically anisotropic molecule. This seems to me a grave objection, notwithstanding that the anisotropy of N is, in general, rather small. But I perceive a more serious objection to the additive law in the following circumstance. In many cases the compound has an entirely different distribution of absorption bands from that of the constituents (elements or not), i. e. *new free frequencies are produced* and the old ones are shifted by combination or dissociation*. The resultant dispersion- and absorption-curves are not obtainable by a superposition of the component ones. In plain language, *colour is produced, or destroyed*, by combination or by dissociation of substances which may themselves be colourless, or nearly so, to the human eye or to the spectrograph. It is hard to understand why this circumstance has been entirely kept out of account in the chemical studies of molecular refractivity. It is true that there is a great chapter in chemistry entitled "Colour and Constitution," but, as far as I can gather, this is treated without any connexion with "Molecular and Atomic Refraction and Dispersion." The existing so-called "theories of colour," due to Witt, Armstrong, Kauffmann, and Baly, have nothing in common with the rich material collected by the refractivitists, the late J. W. Brühl and his followers †.

Enough has now been said to justify an attempt to amplify Lorentz's additive law by taking explicitly into account the electro-optical ‡ interaction of the atoms constituting a molecule. This will occupy our attention in the following sections. The need of a similar investigation has, of course, been felt by physicists, and Lorentz himself says in connexion with Brühl's work (*loc. cit.* p. 150):—"There is at

* And this is closely connected with all the stated facts of huge exaltation of molecular dispersion.

† An account of "Colour and Constitution" is given in *Enc. Brit.* 11th ed. vol. vi. (1910) pp. 70-72. See also Smiles's 'Chemical Constitution and Physical Properties,' Longmans (1910), Chaps. X., XI.

‡ I. e. so far as the *dispersive* electrified particles (electrons, say), and these only, are concerned.

all events an interaction of an electric nature between neighbouring atoms, precisely on account of the displacements of their electrons; there may also be other interactions about whose nature we are as yet entirely in the dark. On these grounds we must expect greater or smaller deviations [from the additive law] from which one may one day be able to draw some conclusions concerning the structure of a molecule." But, as far as I know, no such investigation has been undertaken up to date, no doubt because of the excessive complexity of the problem when treated in its full extent—that is, together with the questions of "valency" and of all the dynamical properties of a molecule considered as a *system of atoms* carrying electrified particles. Nor would I pretend to solve the full problem. But what I propose is a much more modest task, and one which does not seem entirely hopeless or useless, viz.: To investigate, with the simplest assumptions possible, the mutual action of the atoms of a molecule *only so far as the oscillations of their dispersive particles (electrons)* are concerned*, and taking the molecule as being a comparatively *fixed* constellation of the atoms. In short, to treat the optical side of the question detached from all its other aspects. In doing so one is fully aware that such a division of the problem is artificial and physically illegitimate. Yet, the solution of the limited, and therefore easy, problem may turn out to have the value of a first approximation at least, preparing the way for obtaining the successive approximations.

2. Atomic Interaction; General Equations.

Let each of the atoms A_1, A_2 , etc., like or unlike, contain a *single dispersive particle* which (without prejudicing the values of its e, m) will, for the sake of shortness, be called an "electron." Let $-e_1, -e_2$, etc., m_1, m_2 , etc. be the charges and the masses of the electrons contained in A_1, A_2 , etc., and let O_1, O_2 , etc. be the positions of equilibrium of the electrons within their atoms, and $\mathbf{r}_1, \mathbf{r}_2$, etc. the vectorial displacements of the electrons from these positions. We shall assume throughout that all these points O_i , centres—as we may call them—of the atoms contained

* Some of the most authoritative physicists believe to have strong reasons for suspecting that the dispersion electrons have much to do, or even are identical, with the "valency electrons". It may well be so. But, true to my above limitation of the problem, I shall purposely ignore the possible "valency"-rôle of the dispersive particles.

within the same molecule, constitute a *rigid system*, without in the least inquiring into the forces keeping them together. Let, in an isolated atom A_i , the displacement \mathbf{r}_i be counteracted by the usual restitutive force $-m_i\gamma_i\mathbf{r}_i$, so that $n_i = \sqrt{\gamma_i}$ is the *free frequency* (in 2π seconds) of the atom when unmolested by foreign interference. In other words, let the differential equation of motion for the i -th isolated atom be

$$\ddot{\mathbf{r}}_i + \gamma_i\mathbf{r}_i = 0, \quad i = 1, 2, \text{etc.} \quad . \quad . \quad . \quad (3)$$

Thus each atom by itself will be optically isotropic, since $\gamma_i = n_i^2$ is an ordinary scalar.

We shall not introduce explicitly any "friction"-terms, keeping solely in mind that such terms are to be brought in whenever the period of the external agents approaches a free period.

Next, as to the interaction of atoms, in order to proceed any further, we have to make some definite assumption about the electrical properties of the centres O_1, O_2 , etc. We shall choose a possibly simple one, viz., that when the electron $-e_i$ is displaced, the centre O_i behaves as if it were the seat of a point charge $+e_i$, so that an electric doublet is created, of moment $e_i\mathbf{r}_i^*$. And so for every atom. (This does not imply that there are no other charges in the atom, or that the whole atom is electrically neutral. It means only that we are concentrating our attention exclusively upon the dispersive electron and its position of equilibrium.) Again, having once assumed that the centres O_1, O_2 , etc. are fixed with respect to one another, there is no need of contemplating the mutual forces between the charges $+e_1, +e_2$, etc. appearing in O_1, O_2 , etc. Further, the action of O_i upon its own electron can be considered as already contained in the restitutive force $-m_i\gamma_i\mathbf{r}_i$. Thus, the electron of the i -th atom will be acted upon only by all the doublets produced in the remaining atoms of the molecule. (The influence of other molecules being disregarded, of course.) Of this action we shall assume that it is ordinary electrostatic action, which will certainly be the case if the velocities of the oscillating electrons are but small fractions of the light velocity *in vacuo*. Finally, we shall assume that the amplitudes of these oscillations, *i. e.* of \mathbf{r}_i , are small as compared with the mutual distances R_{ij} of the centres O_i, O_j .

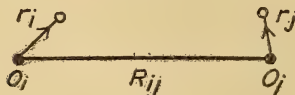
Under these conditions the force on the i -th electron due

* If the reader desires to have a picture of these conditions he may look upon O_i as the centre of Sir J. J. Thomson's "sphere of positive electricity." But this is by no means necessary.

to the j -th atom, playing simply the part of a doublet, will be directed along the line $O_i O_j$ and its intensity will be proportional to the projection of \mathbf{r}_j upon $O_i O_j$.

In fact, let x_i, x_j be the components of the displacements $\mathbf{r}_i, \mathbf{r}_j$ along $O_i O_j$ (fig. 1); then, neglecting squares of r_i/R_{ij} , r_j/R_{ij} , the component of the force on $-e_i$ taken along that direction will be

Fig. 1.



$$X_{ij} = \frac{e_i e_j}{R_{ij}^2} \left[\left(1 - \frac{x_i}{R_{ij}} \right)^{-2} - \left(1 - \frac{x_i - x_j}{R_{ij}} \right)^{-2} \right] = \frac{2e_i e_j}{R_{ij}^3} x_i,$$

while the transversal component will be of higher order. Thus the whole force on the i -th electron due to the j -th atom will be

$$\mathbf{F}_{ij} = \frac{2e_i e_j}{R_{ij}^3} x_j \mathbf{u}_{ij}, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where \mathbf{u}_{ij} is a unit vector from O_i to O_j . And the resultant force \mathbf{F}_i on the i -th electron due to the remaining atoms of the molecule will be the vector sum of all expressions of the type of (4),

$$\mathbf{F}_i = \sum \mathbf{F}_{ij}, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

the summation to be extended over all $j \neq i$. Thus \mathbf{F}_1 will be a linear function of the projections of $\mathbf{r}_2, \mathbf{r}_3$, etc., upon $O_1 O_2, O_1 O_3$, etc., and similarly for \mathbf{F}_2 , and so on. Thus, taking account of the atomic interaction, we shall have, instead of (3), for a molecule consisting of κ atoms, κ linear differential equations:

$$\ddot{\mathbf{r}}_i + \gamma_i \mathbf{r}_i - \frac{1}{m_i} \mathbf{F}_i = 0, \quad i = 1, 2, \dots, \kappa. \quad . \quad . \quad (6)$$

The molecule as such will now have, generally speaking, 3κ new free frequencies, optically relevant, instead of the original ones, $\sqrt{\gamma_i}$.

Finally, let us imagine a body composed of a large number of such molecules. Let \mathfrak{N} be their number per unit volume, and \mathbf{E} an external electric field, *e.g.*, the electric force in an incident wave of light. Then, precisely as in the

usual theory of dispersion (Lorentz, *loc. cit.* p. 139), the external force acting on our i -th electron will be

$$e_i(\mathbf{E} + a\mathbf{P}),$$

where a is Lorentz's $\frac{1}{3} + s$, and may for the present be simply taken equal to $\frac{1}{3}$, and \mathbf{P} , the electric polarization of the body, is the average of $\mathfrak{N}(e_1\mathbf{r}_1 + e_2\mathbf{r}_2 + \dots + e_\kappa\mathbf{r}_\kappa)$ taken over a physically small volume, but containing a sufficiently large number of molecules, *i. e.*

$$\mathbf{P} = \mathfrak{N}(e_1\bar{\mathbf{r}}_1 + e_2\bar{\mathbf{r}}_2 + \dots + e_\kappa\bar{\mathbf{r}}_\kappa) = \mathfrak{N}\Sigma e_i\bar{\mathbf{r}}_i. \quad (7)$$

Now, \mathbf{D} being the (macroscopic) dielectric displacement, we have $\mathbf{D} = K\mathbf{E} = \mathbf{E} + \mathbf{P}$, where, for periodic oscillations,

$$K = \mu^2;$$

the "dielectric constant" or the permittivity K being in general, for anisotropic bodies, a linear *vector operator*, and for isotropic bodies an ordinary scalar. Thus the external force on the i -th electron becomes

$$e_i[1 + a(K - 1)]\mathbf{E},$$

and with $a = \frac{1}{3}$, *i. e.*, strictly for regular cubical distribution of molecules*, and approximately for various other cases,

$$\frac{1}{3}e_i(K + 2)\mathbf{E}.$$

Dividing this force by m_i and introducing it on the right hand of (6) we have the κ equations

$$\ddot{\mathbf{r}}_i + \gamma_i\dot{\mathbf{r}}_i - \frac{1}{m_i}\mathbf{F}_i = \frac{1}{3}\frac{e_i}{m_i}(K + 2)\mathbf{E}. \quad (8)$$

For monochromatic incident light of frequency $n = 2\pi c/\lambda$ (in 2π seconds) the electric force \mathbf{E} and all the vectors \mathbf{r} are proportional to e^{int} , $i = \sqrt{-1}$, so that $\ddot{\mathbf{r}} = -\gamma\mathbf{r}$, where $\gamma = n^2$. Thus we obtain, for a substance composed of κ -atomic molecules,

$$(\gamma_i - \gamma)\mathbf{r}_i - \frac{1}{m_i}\mathbf{F}_i = \frac{1}{3}\frac{e_i}{m_i}(K + 2)\mathbf{E}; \quad i = 1, 2, \dots, \kappa. \quad (9)$$

* This concerns the distribution of points, of which each is the representative of a molecule as a whole, and does not necessarily imply parallelism of orientation of such lines as O_1O_2 or O_2O_3 , etc.; the latter will be the case only in (optically) crystalline bodies. On the other hand we may have, say, a strictly cubic arrangement, but with a haphazard distribution of directions of O_1O_2 , etc.; then the body will be optically isotropic.

Since the forces \mathbf{F}_i , to be constructed on the type of (4), (5), are all linear vector functions of the \mathbf{r} 's, we have in (9) a system of κ linear vector equations for as many vectors \mathbf{r}_i . On the other hand we have, by (7),

$$(K-1)\mathbf{E} = \Re \sum e_i \bar{\mathbf{r}}_i. \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Introducing here the \mathbf{r} 's to be found from (9) as linear functions of $(K+2)\mathbf{E}$, we shall obtain the refractivity operator

$$\omega = 3 \frac{K-1}{K+2}, \quad . \quad . \quad . \quad . \quad . \quad (11)$$

which in the simplest case of isotropy reduces to the familiar expression $3(\mu^2-1)/(\mu^2+2)$. Our above N , the molecular refractivity-operator, will be $N = \frac{1}{3} M \omega / d$. The operator ω will obviously contain, in the denominator, the determinant of the equations (6) of the molecule under no external forces, thus bringing into evidence the free frequencies and, therefore, the absorption bands of the compound, and, in fact, all of its optical properties in terms of the attributes of the atoms and of their configuration within the molecule. This will be developed in detail on the particular examples of two- and three-atomic molecules, which will pave the way for the treatment of polyatomic ones. The operator ω will have, in general, three different principal values, and will, in the case of a haphazard orientation of the molecules, degenerate into an ordinary scalar magnitude.

The equations (9) and (10), with the forces \mathbf{F}_i defined by (4), (5), will be our fundamental system of equations, to be developed in each particular case.

Notice that with increasing mutual distances (R_{ij}) of the atoms all the interatomic forces \mathbf{F}_i tend to evanescence, and (9) are at once reduced to the ordinary equations of the Lorentz theory, as it should be. In that limiting case we have from (9), calling x_i the projection of \mathbf{r}_i upon any fixed direction whatever, $(\gamma_i - \gamma)x_i = \frac{1}{3} \frac{e_i}{m_i} (K+2)E_x$, so that K , and therefore ω , obviously becomes an ordinary scalar (the substance becomes optically isotropic) and its value is, by (10),

$$\omega \equiv 3 \frac{K-1}{K+2} = \omega_1 + \omega_2 + \dots + \omega_\kappa,$$

where

$$\omega_i = \Re \frac{e_i^2 / m_i}{\gamma_i - \gamma}, \quad . \quad . \quad . \quad . \quad . \quad (12)$$

as in Lorentz's theory, and therefore also

$$N = N_1 + N_2 + \dots + N_\kappa.$$

Thus the additive law of refractivities appears, of course, as the limiting case for evanescent atomic interaction.

Our supplementary terms concentrated in \mathbf{F}_i bring in optical anisotropy (when not destroyed by haphazard orientations of the molecules) and non-additivity, modifying at the same time the free frequencies and, therefore, also the position of the absorption bands. The quantitative aspect of this departure from additivity will be discussed and illustrated in the following sections.

3. Diatomic Molecules,

Let x_1, x_2 be the *axial* components of $\mathbf{r}_1, \mathbf{r}_2$, *i. e.* their projections on O_1O_2 , and y_1, y_2 their transversal components. The forces $\mathbf{F}_1, \mathbf{F}_2$ being purely axial, the latter components are not modified by the atomic interaction. Thus the transversal component of (9) gives

$$e_1 y_1 = \frac{e_1^2 (K_s + 2) E_s}{3 m_1 (\gamma_1 - \gamma)}; \quad e_2 y_2 = \frac{e_2^2 (K_s + 2) E_s}{3 m_2 (\gamma_2 - \gamma)}, \quad . \quad (13 s)$$

and the axial component, by (4),

$$\left. \begin{aligned} (\gamma_1 - \gamma) e_1 x_1 - \frac{2 e_1^2}{m_1 R^3} e_2 x_2 &= \frac{1}{3} \frac{e_1^2}{m_1} (K_a + 2) E_a \\ - \frac{2 e_2^2}{m_2 R^3} e_1 x_1 + (\gamma_2 - \gamma) e_2 x_2 &= \frac{1}{3} \frac{e_2^2}{m_2} (K_a + 2) E_a \end{aligned} \right\}, \quad (13 a)$$

where R is the mutual distance of the centres O_1, O_2 , and the suffixes a, s are used to distinguish between the axial and the transversal directions. O_1O_2 will shortly be called *the axis* of the molecule. The above equations have to be combined with (10). In doing so we shall consider separately the two important cases: 1) when the axes of all the molecules are parallel to one another, and 2) when their orientation is haphazardly distributed throughout the substance. The first case will correspond to an optically anisotropic, and the second to an isotropic substance. From our present point of view the first case is the more important one, since it reproduces the properties of the molecule as such, while in the second case these properties are partly obliterated by averaging through the crowd of molecules.

Anisotropic Body.—All the axes being parallel to one another we have simply $\bar{\mathbf{r}}_i = \mathbf{r}_i$, *i. e.* $\bar{x}_i = x_i, \bar{y}_i = y_i$, and

therefore, by (10) and (13 s), writing $e_1^2/m_1=B_1$, $e_2^2/m_2=B_2$,

$$\omega_s = 3 \frac{K_s - 1}{K_s + 2} = \mathfrak{N} \frac{B_1}{\gamma_1 - \gamma} + \mathfrak{N} \frac{B_2}{\gamma_2 - \gamma} = \omega_1 + \omega_2, \quad (14 s)$$

that is to say, *the transversal refractivity is purely additive*. This is simply the result of the axiality of interaction, based on our assumption, made at the beginning, that the second and the higher powers of (r_1/R) , (r_2/R) are negligible. Passing on to the axial direction we have in (13 a) two linear equations for e_1x_1 , e_2x_2 . Let D be the determinant of these equations, i. e.

$$D = (\gamma - \gamma_1)(\gamma - \gamma_2) - \frac{4B_1B_2}{R^3}. \quad . \quad . \quad . \quad (15)$$

Then, introducing e_1x_1 , e_2x_2 from (13 a) into

$$(K_a - 1)E_a = \mathfrak{N}(e_1x_1 + e_2x_2),$$

the axial component of (10), we have

$$\omega_a = \frac{\mathfrak{N}}{D} \left[B_1(\gamma_2 - \gamma) + B_2(\gamma_1 - \gamma) + \frac{4B_1B_2}{R^3} \right],$$

or, in terms of the atomic attributes ω_1 , ω_2 ,

$$\omega_a = \frac{\omega_1 + \omega_2 + 4\omega_1\omega_2/\mathfrak{N}R^3}{1 - 4\omega_1\omega_2/\mathfrak{N}^2R^6}. \quad . \quad . \quad . \quad (14 a)$$

Thus, the *axial refractivity*, unlike the transversal one, shows an essential departure from additivity, and this is of such a nature that the difference $\omega_a - (\omega_1 + \omega_2)$ cannot obviously be thrown either upon the first or upon the second, nor partly upon the first and partly upon the second of the constituent atoms. Any such splitting of terms containing the product $\omega_1\omega_2$ and the mutual distance of the atoms would be entirely artificial. Thus far the qualitative aspect of the matter. And as concerns its quantitative side, notice that, in a true molecule, the departure from the additive law cannot be negligible and will, in most cases, be very considerable. In fact, \mathfrak{N} is the number of (diatomic) molecules per unit volume, and therefore $\mathfrak{N}R^3$ the number of molecules per cube whose edge is the mutual distance of the atomic centres. Now if the system of each pair of atoms deserves at all the name of a molecule, R is certainly not greater than the average mutual distance of molecules. Thus the (pure) number $\mathfrak{N}R^3$ is certainly not greater than unity, and in most cases even a fraction only.

Therefore, as long as the molecule is not, to all purposes, thoroughly dissociated, neither ω_1/\mathfrak{NR}^3 , ω_2/\mathfrak{NR}^3 , nor the product of these ratios, appearing in the denominator of (14 a), can be neglected in presence of ω_1 and ω_2 themselves.

Notice that, ω_s obeying the additive law, the contribution due to interatomic cooperation alone can be written, by (14 a),

$$\omega_a - \omega_s = \frac{4\omega_1\omega_2}{\mathfrak{NR}^3} \cdot \frac{1 + (\omega_1 + \omega_2)/\mathfrak{NR}^3}{1 - 4\omega_1\omega_2/\mathfrak{N}^2\mathfrak{R}^6}. \quad (14)$$

The expression (14 a) given above has seemed interesting, inasmuch as it exhibits the connexion with (and at the same time the departure from) the traditional law of additivity. But this having once been noted, there is another, mathematically equivalent, form of the axial molecular refractivity which seems a great deal more interesting, since it brings into evidence the *new natural or free frequencies* of the molecule as distinguished from those ($\sqrt{\gamma_1}$, $\sqrt{\gamma_2}$) belonging to the atoms when uncombined. In fact, returning to the intermediate form, written just before (14 a), notice that the squares of the new natural frequencies, let us say γ' , γ'' , are the roots of the quadratic equation

$$D = 0.$$

Thus we can write $D = (\gamma' - \gamma)(\gamma'' - \gamma)$, and therefore

$$\omega_a = \mathfrak{N} \frac{B_1(\gamma_2 - \gamma) + B_2(\gamma_1 - \gamma) + 4B_1B_2/\mathfrak{R}^3}{(\gamma' - \gamma)(\gamma'' - \gamma)},$$

which is, essentially, the required form.

When this is split into partial fractions we obtain ultimately, writing again (14 s) for the sake of completeness, the following expressions for the transversal and the axial refractivity :

$$\left. \begin{aligned} \omega_s &= \mathfrak{N} \left[\frac{B_1}{\gamma_1 - \gamma} + \frac{B_2}{\gamma_2 - \gamma} \right] \\ \omega_a &= \mathfrak{N} \left[\frac{B'}{\gamma' - \gamma} + \frac{B''}{\gamma'' - \gamma} \right] \end{aligned} \right\}, \quad \dots \quad (16)$$

where the constant coefficients B' , B'' are determined by

$$\left. \begin{aligned} (\gamma' - \gamma'') \cdot B' &= B_1(\gamma' - \gamma_2) + B_2(\gamma' - \gamma_1) - \frac{4B_1B_2}{\mathfrak{R}^3} \\ (\gamma' - \gamma'') \cdot B'' &= B_1(\gamma_2 - \gamma'') + B_2(\gamma_1 - \gamma'') + \frac{4B_1B_2}{\mathfrak{R}^3} \end{aligned} \right\}. \quad (17)$$

Thus, in ω_a as compared with ω_s , the old free frequencies $\sqrt{\gamma_1}$, $\sqrt{\gamma_2}$ (and, therefore, absorption bands) are replaced by new ones, $\sqrt{\gamma'}$, $\sqrt{\gamma''}$, and the old coefficients B_1 , B_2 are replaced by new ones, B' , B'' . The forms of the corresponding dispersion curves, with, say, γ as abscissæ and ω_s , ω_a as ordinates, are entirely different; the first of them only being a superposition of the atomic dispersion curves, while the second is profoundly modified, to wit, not only in its coefficients but also with respect to the position of its singularities. As to these latter, γ' , γ'' are the roots of $D=0$, i. e. by (15),

$$\gamma'_{\gamma''} = \frac{1}{2}(\gamma_1 + \gamma_2) \mp \frac{1}{2} \sqrt{(\gamma_1 - \gamma_2)^2 + 16B_1B_2/R^6}. \quad (18)$$

Thus, even if both γ_1 , γ_2 are in the extreme ultraviolet, γ' may well be thrown into the accessible region of the spectrum. Of this more will be said in the next section. The formulæ (16) and (17), with (18), complete the solution of the problem in hand. If \mathbf{i} is a unit vector along the axis, the whole refractivity-operator can be written $\omega = \omega_s + \omega_a \mathbf{i} \cdot \mathbf{i}$, where $\mathbf{i} \cdot \mathbf{i}$ is a dyad. The corresponding permittivity-operator will be $K = K_s + K_a \mathbf{i} \cdot \mathbf{i}$. The resulting crystal will have *one optical axis* coinciding with the parallel axes \mathbf{i} of the molecules. In common optical terminology,

$\mu_s = \sqrt{K_s}$ will be *the ordinary*,

and $\mu_a = \sqrt{K_a}$ *the extraordinary* refractive index of the uniaxial crystal. And if M is the molecular weight and d the density of the crystal,

$$N_s = \frac{1}{3} \frac{M}{d} \omega_s, \quad N_a = \frac{1}{3} \frac{M}{d} \omega_a, \quad \dots \quad (19)$$

will be its ordinary and extraordinary molecular refractivity, respectively. Thus (16) will read: *the ordinary molecular refractivity is additive, and the extraordinary non-additive or "constitutive."*

Notice that, by (17) and (18), we have

$$\begin{aligned} & B' + B'' = B_1 + B_2 \} \\ \text{and} \quad & \gamma' + \gamma'' = \gamma_1 + \gamma_2 \} \end{aligned} \quad \dots \quad (20)$$

i. e. *the sum of the dispersion coefficients, and the sum of the squared free frequencies* of the diatomic molecule have the remarkable property of being *invariant* with respect to

atomic interaction. This is a sort of compensation for the disappearance of the ordinary law of additivity.

Subcase: Equal Atoms.—If the two atoms compounding the molecule are equal, *i. e.* when $e_1^2/m_1 = e_2^2/m_2 = B_1 = B_2 = B$ and $\gamma_1 = \gamma_2 = \gamma_0$, so that $n_0 = \sqrt{\gamma_0}$ is the frequency belonging to each atom, then we have, by (16), (17), and (18),

$$\omega_s = \frac{2B\mathfrak{N}}{\gamma_0 - \gamma}; \quad \omega_a = \frac{2B\mathfrak{N}}{\gamma' - \gamma}, \quad . \quad . \quad . \quad . \quad (21)$$

where

$$\gamma' = \gamma_0 - \frac{2B}{R^3}. \quad . \quad . \quad . \quad . \quad . \quad (22)$$

Notice that in the present case $B' = 2B$ and $B'' = 0$, so that the second new free frequency given by $\gamma'' = \gamma_0 + 2B/R^3$, does not enter at all into the refractivity of the compound. The axial refractivity ω_a has the same coefficient as the transversal one, but its singularity (absorption band) γ' is shifted away from γ_0 towards the red, since B and R are essentially positive. The absorption band of both (equal) constituents being, say, in the extreme ultraviolet, the new band of the molecule may well fall into the visible region of the spectrum.

In order not to interrupt the general course of ideas, illustrative numerical examples will be given separately, in Section 4. Here it will be enough to note that a crystal composed even of the simplest kind of molecules, namely diatomic ones, would show, by the above formulæ, the remarkable phenomenon known under the name of *dichroism*. And when we come to consider more complicated molecules we shall perceive the possibility of accounting for *pleochroism* as well. Let us now pass on to the second of the two cases mentioned above.

Isotropic Body.—The kind of isotropy we have in mind is *optical* isotropy, of course*. Let, therefore, the directions of the axes of our diatomic molecules be haphazardly distributed, so that no particular direction is privileged. Then, for each individual molecule, we have still the formulæ (13 s), (13 a) with K_s, K_a replaced by the macroscopically

* The body may well be a crystal in the mineralogical sense of the word and yet, like rock-salt, show no traces of optical anisotropy. Such will be the case if the molecules are distributed, say, in three cubic space lattices with the axes of the molecules mutually perpendicular, so that the molecular anisotropy will be macroscopically obliterated.

observable $K = \mu^2$, that is, writing again $e_1^2/m_1 = B_1$ and $e_2^2/m_2 = B_2$,

$$\left. \begin{aligned} (\gamma_1 - \gamma) e_1 x_1 - \frac{2B_1}{R^3} e_2 x_2 &= \frac{1}{3} B_1 (K + 2) E_a, \\ - \frac{2B_2}{R^3} e_1 x_1 + (\gamma_2 - \gamma) e_2 x_2 &= \frac{1}{3} B_2 (K + 2) E_a, \end{aligned} \right\}$$

$$(\gamma_1 - \gamma) e_1 y_1 = \frac{1}{3} B_1 (K + 2) E_s; \quad (\gamma_2 - \gamma) e_2 y_2 = \frac{1}{3} B_2 (K + 2) E_s,$$

where x_1, y_1 and x_2, y_2 are the components of \mathbf{r}_1 and \mathbf{r}_2 along and perpendicular to the individual molecular axis \mathbf{i} , in the plane \mathbf{E}, \mathbf{i} , and E_a, E_s the components of the external electric vector \mathbf{E} along and perpendicularly to the axis. Let that molecular axis make with the (fixed) direction of \mathbf{E} the angle θ . Then $E_a = E \cos \theta$, $E_s = E \sin \theta$, and

$$e_1 x_1 = \frac{B_1 (K + 2)}{3D} \left(\gamma_2 - \gamma + \frac{2B_2}{R^3} \right) E \cos \theta;$$

$$e_1 y_1 = \frac{B_1 (K + 2)}{3(\gamma_1 - \gamma)} E \sin \theta,$$

with similar expressions for $e_2 x_2, e_2 y_2$. The vector $e_1 \bar{\mathbf{r}}_1 + e_2 \bar{\mathbf{r}}_2$, to be substituted in (10), falls into the direction of \mathbf{E} , and its tensor is $e_1 (x_1 \cos \theta + y_1 \sin \theta) + e_2 (x_2 \cos \theta + y_2 \sin \theta)$. Thus we have, by (10),

$$\begin{aligned} \omega = \frac{\Re}{D} \left\{ B_1 (\gamma_2 - \gamma) + B_2 (\gamma_1 - \gamma) + \frac{4B_1 B_2}{R^3} \right\} \overline{\cos^2 \theta} \\ + \Re \left\{ \frac{B_1}{\gamma_1 - \gamma} + \frac{B_2}{\gamma_2 - \gamma} \right\} \overline{\sin^2 \theta}, \end{aligned}$$

that is, comparing with our former expressions for ω_s, ω_a ,

$$\omega = \omega_s \overline{\sin^2 \theta} + \omega_a \overline{\cos^2 \theta}.$$

The latter result could also be obtained at once by considering $\omega = \omega_s + \omega_a \mathbf{i} \cdot \mathbf{i}$ as the operation to which \mathbf{E} is subjected.

Now, the average of $\cos^2 \theta$ is $1/3$ and that of $\sin^2 \theta$ is $2/3$, so that we have, ultimately, for an isotropic diatomic substance,

$$\omega = \frac{2}{3} \omega_s + \frac{1}{3} \omega_a, \quad . \quad . \quad . \quad . \quad . \quad (23)$$

where ω_s, ω_a are as before. If their form (14) is used, then

$$\omega = \frac{2}{3}(\omega_1 + \omega_2) + \frac{1}{3} \frac{\omega_1 + \omega_2 + 4\omega_1\omega_2/\mathfrak{N}R^3}{1 - 4\omega_1\omega_2/\mathfrak{N}^2R^6}, \quad (24)$$

and if the form (16) is used, in which the natural frequencies are brought into evidence, then

$$\mathfrak{N} = \frac{2}{3} \left(\frac{B_1}{\gamma_1 - \gamma} + \frac{B_2}{\gamma_2 - \gamma} \right) + \frac{1}{3} \left(\frac{B'}{\gamma' - \gamma} + \frac{B''}{\gamma'' - \gamma} \right), \quad (25)$$

where B', B'' and γ', γ'' are as in (17) and (18). Thus the dispersion curve of an isotropic diatomic substance has *four* singularities (to which as many absorption bands will correspond), two inherent in the atoms, γ_1, γ_2 , and two more, γ', γ'' , due to their interaction. In general, therefore, the dispersion curve will be profoundly modified by the atomic interaction.

Subcase: Equal Atoms.—In this case we have $\gamma_1 = \gamma_2 = \gamma_0$, $B_1 = B_2 = B$, and $B' = 2B$, $B'' = 0$, as has been shown before, so that (24) becomes

$$\omega = \frac{4}{3}\omega_0 + \frac{2}{3} \frac{\omega_0}{1 - 2\omega_0/\mathfrak{N}R^3}, \quad (24a)$$

and (25),

$$\left. \begin{aligned} \mathfrak{N} &= \frac{2}{3}B \left(\frac{2}{\gamma_0 - \gamma} + \frac{1}{\gamma' - \gamma} \right), \\ \gamma' &= \gamma_0 - 2B/R^3. \end{aligned} \right\} \quad (25a)$$

The molecular refractivity, $N = \frac{1}{3}M\omega/d$, of such a substance will have two singularities: one at $\gamma = \gamma_0$ belonging to each of the atoms, and another at $\gamma = \gamma'$, which is always $< \gamma_0$ and is due to the mutual action of the atoms.

Notice that the denominator in (24a) vanishes (ω becomes infinite and K imaginary) for $\mathfrak{N}R^3 = 2\omega_0$, that is, by (12), for $R^3 = 2B/(\gamma_0 - \gamma)$, *i. e.* precisely for $\gamma = \gamma'$. Thus, keeping the incident frequency $\sqrt{\gamma}$ constant and varying R^* , we shall have to remember that approaching the particular distance

$$R' = \left(\frac{2\omega_0}{\mathfrak{N}} \right)^{1/3} \quad (26)$$

means that $\sqrt{\gamma}$ is approaching the natural frequency $\sqrt{\gamma'}$ of the molecule, when the omitted "friction" terms must be taken into account. In short, for that *singular distance* we

* As in an example to be given in the next Section.

have selective absorption. The same is the case when γ_0 (which is independent of R) is approached, for then ω_0 itself, and therefore the first term in (24 a) becomes infinite. This singular rôle of γ_0 and γ' is shown explicitly in (25 a), which is but another form of (24 a).

For the numerical application of our formulæ to the molecular and the atomic refractivities as usually defined, it will be well to write at least the last two ones in terms of N instead of ω . Remember that, by definition,

$$\omega/N = 3d/M = 3\mathfrak{N}m_H : 1.008,$$

where m_H is the absolute mass of a hydrogen atom, $1.64 \cdot 10^{-24}$ gr., so that

$$\omega/\mathfrak{N} = \alpha N,$$

and similarly,

$$\omega_1/\mathfrak{N} = \omega_2/\mathfrak{N} \equiv \omega_0/\mathfrak{N} = \alpha N_0,$$

where α is the constant

$$\alpha = \frac{3m_H}{1.008} = 4.88 \cdot 10^{-24} \text{ gr.} \quad . \quad . \quad . \quad (27)$$

Thus (24 a) becomes

$$N = \frac{4}{3} N_0 + \frac{2}{3} \cdot \frac{N_0}{1 - 2\alpha N_0/R^3}, \quad . \quad . \quad . \quad (24 b)$$

and (25 a),

$$\left. \begin{aligned} N &= \frac{2B}{3\alpha} \left(\frac{2}{\gamma_0 - \gamma} + \frac{1}{\gamma' - \gamma} \right), \\ \gamma' &= \gamma_0 - 2B/R^3. \end{aligned} \right\} \quad . \quad . \quad . \quad (25 b)$$

Finally, we have for the singular distance, as a function of the incident frequency $\sqrt{\gamma}$,

$$R' = (2\alpha N_0)^{1/3}, \quad . \quad . \quad . \quad . \quad (26 a)$$

where N_0 is a known function of γ , viz. $B/\alpha(\gamma_0 - \gamma)$. It will be remembered that B stands for the constant e^2/m .

4. *Formulæ for Diatomic Substances discussed and illustrated.*

Before passing on to the considerably more complicated case of triatomic molecules, it will be well to discuss somewhat further the refraction formulæ obtained in the last Section and, possibly, to make in this connexion some

remarks concerning the chemist's table of atomic refractivities and dispersivities. If not otherwise stated, we shall assume, throughout this Section, an *optically isotropic* substance.

Molec. Refractivity and Interatomic Distance.—Let us consider two diatomic substances, S_1 and S_2 , whose molecules consist of the same atoms, but placed from one another in different distances, R_1 for the first, and $R_2 = R_1 + \Delta R$ for the second substance, where ΔR may have any finite value. Let ΔN be the corresponding difference of the molecular refractivities, N' and N'' , of these substances. We shall consider here the simplest case of two *equal atoms*, each having the atomic refractivity N_0 , a known function of γ :

$$N_0 = \frac{B/\alpha}{\gamma_0 - \gamma}.$$

Thus, by (24 b), using the singular distance R' given by (26 a),

$$N' = \frac{2N_0}{3} \left[2 + \frac{1}{1 - (R'/R_1)^3} \right]; \quad N'' = \frac{2N_0}{3} \left[2 + \frac{1}{1 - (R'/R_2)^3} \right].$$

. . . (28)

Let us remember that N_0 would be the refractivity of a strictly monoatomic substance, S_0 , of the element in question. If such a substance, as well as the two different kinds of diatomic substances, S_1 , S_2 , of the same element, were available for refractometric examination, then it would be possible to derive from the observed N_0 , N' , N'' , by means of the above formulæ, some information about the interatomic distances R_1 and R_2 in the molecules of the substances S_1 and S_2 . But no such actual data being available at present, we must content ourselves with a provisional, and to a certain extent ideal, and arbitrarily constructed, numerical example which may, none the less, afford an instructive illustration of the general formulæ.

Let our atoms be the carbon atoms and let us suppose, for the sake of argument, that there is a substance in whose molecules the group C—C (with "single bond") occurs, possibly among other atoms of any kind, such, however, that their total influence on that group is negligible*. For

* This clause is indispensable, for there is, of course, no such substance as C_2 . We could take hydrogen which does exist as H_2 , *i. e.* as $H-H$, in ordinary hydrogen gas, but this would give us no opportunity of considering the huge extra-term [= of Land-Börn's table. And then we know nothing about the optical properties of monoatomic hydrogen.

the sake of shortness of language, we shall speak of S_1 simply as of the substance C-C. Similarly, let S_2 be the substance C=C, with "double bond." Let, as above, N' be the molecular refractivity of the former, and N'' that of the latter, say, for sodium light, that is, by Landolt-Börnstein's Table (all N 's being in $\text{cm}^3 \text{gr}^{-1}$),

$$N' = 4.836; \Delta N = 1.733; N'' = 6.569, \quad . \quad . \quad (A)$$

always assuming, of course, that these cases are such as not to call for other extra-terms besides that due to the double bond. Next, let N_0 be the atomic refractivity of carbon. At first one might be tempted to take for N_0 the C of that table, *i. e.* 2.418 (the half of N'), because this is the smallest carbon-refractivity quoted by chemists. But, apart from other reasons, there is a considerably smaller one which, moreover, seems to have better claims to be *the* atomic refractivity of carbon than 2.418, which is derived from rather complicated organic compounds. In fact, it has seemed interesting to see what that refractivity is like when it is calculated from purest carbon as found in nature, *viz.* from *diamond*. Now, Martens (as quoted in Landolt-Börnstein's *Tafeln*) finds for the refr. index of diamond, for the D-line ($\lambda = 589$), at 14°C ., the value $\mu = 2.4172$, and the density of that crystal can be taken equal to 3.51. From these data I find

$$N_{\text{diam.}} = \frac{4.8429 \cdot 12}{7.8429 \cdot 3.51} = 2.111.$$

This is as much as 0.307 *below* the chemist's fundamental C-value. I am fully aware that this circumstance is not, by itself, a sufficient reason for taking the diamond-value as the true atomic refractivity of carbon. For one could speak here of "depression" due to the mutual linkage of the carbon atoms in diamond. According to Bragg* each carbon atom in diamond is "linked up to the four carbon atoms surrounding it" and placed at the corners of a regular tetrahedron whose centre is occupied by the atom in question,—this being the simplest way of considering the originally double-lattice structure of the crystal as revealed by the X-ray spectrometer. Thus, the difference 0.307 could well be considered as a negative "exaltation" due

* See W. H. and W. L. Bragg's admirable book on 'X Rays and Crystal Structure,' London, Bell (1915), p. 106.

to the influence of those four nearest neighbours, and there would certainly be no cogent reason for declaring the diamond-value as the atomic refractivity N_0 . But, in absence of better knowledge, let us tentatively *assume that the diamond-refractivity is the true atomic refractivity of carbon**, i. e. that, in general, $N_0 = N_{\text{diam.}}$, and therefore, for the D-line,

$$N_0 = 2.111. \quad . \quad . \quad . \quad . \quad . \quad . \quad (B)$$

It is interesting, at any rate, to see what values follow from this assumption, and from (A), for the distances R_1 and R_2 . Now, resolving (28) with respect to R_1 , R_2 , we have

$$\frac{R_1}{R'} = \left(\frac{N' - \frac{4}{3}N_0}{N' - N_0} \right)^{1/3}, \quad \frac{R_2}{R'} = \left(\frac{N'' - \frac{4}{3}N_0}{N'' - N_0} \right),$$

where "the singular distance" R' is as in (26 *a*). Inserting N_0, N', N'' from (A), (B), we find, first of all,

$$R_1 = 0.9052 R' ; \quad R_2 = 0.9443 R',$$

i. e. both distances smaller than the singular distance, for the D-line, and $R_1 < R_2$. Next, to obtain both distances in absolute measure, we have, by (26 a) and (27),

$$R^3 = 2\alpha N_0 = 9.76 \cdot 2.111 \cdot 10^{-24} \text{ cm}^3,$$

that is, $R' = 2.742 \cdot 10^{-8}$, or, in round figures, $R' = 2.74 \text{ \AA.U.}$

Ultimately, therefore, we should have, for the interatomic distances in C-C and in C=C, respectively,

$$R_1=2.481, \quad R_2=2.588 \text{ \AA.U.}$$

These seem quite reasonable figures, being of the order of "molecular dimensions." Also the circumstance that R_1 is somewhat smaller than R_2 seems to harmonize with the phenomenal correlatives of a simple and a double bond. In short, the result would be that in $C-C$ the atoms are somewhat closer packed than in $C=C$. And the inconspicuous increase of their distance by $\Delta R = 0.107 \text{ \AA.U.}$ would be sufficient to account for the huge extra-term $|=$, that is, in the case of sodium light, for $\Delta N = 1.733$.

* This would amount to assuming that the disturbing actions of the four neighbours compensate one another, and such an assumption harmonizes with the optical isotropy of diamond.

Similarly I find, for the interatomic distance R_3 in $C \equiv C$, taking $N''' = N' + |\equiv = 4.836 + 2.398 = 7.234$ (again for the D-line),

$$R_3 = 0.9519 R' = 2.610 \text{ \AA.U.},$$

i.e. again somewhat greater than R_2 . Thus $R_1 < R_2 < R_3$, and the minute increase of distance by

$$\Delta R = R_3 - R_2 = 0.022 \text{ \AA.U.}$$

accounts for the considerable difference

$$\Delta N = |\equiv \text{ minus } | = 0.665.$$

The above values of R_1 , R_2 and R_3 have been calculated, by means of the formula

$$R/R' = \left(\frac{N - \frac{4}{3}N_0}{N - N_0} \right)^{1/3}; \quad R' \equiv (2\alpha N_0)^{1/3}, \quad . \quad (29)$$

from the values of N and N_0 for the D-line. If our theory of atomic interaction (and the provisional assumption that $N_0 = N_{\text{diamond}}$) is correct, then the values of N and N_0 corresponding to other wave-lengths should lead to the same values of R_1 , R_2 , R_3 , or nearly so. Now, taking N (*i.e.* N' , N'' , N''') for the lines H_α , H_β , H_γ from Land-Börn.'s table, and N_0 from observations on diamond*, I find, by means of (29), the results which, together with those obtained a moment ago for the D-line, are collected in the following table. All figures are in Å.U.

| Calc. from | $R_1(c-c).$ | $R_2(c=c).$ | $R_3(c \equiv c).$ |
|------------------|-------------------|-------------------|--------------------|
| H_α | 2.48 ₀ | 2.58 ₅ | 2.60 ₆ |
| D | 2.48 ₁ | 2.58 ₈ | 2.61 ₀ |
| H_β | 2.48 ₃ | 2.59 ₈ | 2.61 ₈ |
| H_γ | 2.49 ₆ | 2.60 ₅ | 2.61 ₇ |

This seems, in view of the roughness of the chemico-optical data, quite satisfactory. There is but a very slight systematic increase of the R_1 , R_2 , R_3 values from the red to the violet line. The result contained in the above table

* *I.e.* $\mu = 2.4100, 2.4354, 2.4511$ for $H_\alpha, H_\beta, H_\gamma$ respectively, whence the corresponding values of N_0 : 2.105, 2.126, 2.138.

can also be expressed by saying that the expression

$$N_0 \frac{N - \frac{4}{3}N_0}{N - N_0}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (30)$$

(quite apart from its meaning as the cube of $R/2\alpha$) is very nearly *free from dispersion*. For the present we shall content ourselves with the above examples, as an illustration of formula (29), which is an inversion of (24 b) or of (28).

Free Frequencies and Interatomic Distance. Limit of Stability.—Turning now to the form (25 b) of the molec. refractivity, for the case of equal atoms, let us consider the dependence of the new free frequency $\sqrt{\gamma'}$ on the intrinsically atomic one, $\sqrt{\gamma_0}$, and on the interatomic distance,

$$\gamma' = \gamma_0 - 2B/R^3,$$

where $B = e^2/m$ is a constant attribute of the dispersive particles. When R decreases, γ' becomes smaller and smaller, that is to say, the “new” absorption band, due to interaction, moves farther and farther away from the old one towards the red or the infra-red end of the spectrum. When R becomes so small that $2B/R^3 = \gamma_0$, we have $\gamma' = 0$, *i. e.* the corresponding free period T' and the wave-length $\lambda' = cT'$ become infinite. When R becomes still smaller, then $\gamma' < 0$, that is, $n' = \sqrt{\gamma'}$ becomes imaginary and the oscillatory function $e^{in't}$ degenerates into an aperiodic one. The electric particles cease to oscillate round their atomic centres. In other words, the system becomes unstable, namely, as regards axial displacements of the electric particles*.

Thus, to the particular distance

$$R_c = \left(\frac{2B}{\gamma_0} \right)^{1/3}$$

corresponds the limit of *optical stability* of the molecule,—“optical,” *i. e.* so far as the dispersive particles are concerned†. In view of this property we shall call R_c the

* The frequency of transversal oscillations is always $\sqrt{\gamma_0}$, independent of R , under the express condition that higher powers of (r_1/R) , (r_2/R) are negligible. The second new frequency

$$\sqrt{\gamma''} = \sqrt{\gamma_0 + 2B/R^3}$$

is always real.

† This may well be accompanied by other profound modifications of the molecule as a system of atoms, but, as has been said in Section 1, all such questions are beyond the scope of the present investigation.

critical distance *. It is that distance at which the restitutive force is just balanced by the interatomic one. For $R < R_c$ the higher powers of (r_i/R) are, of course, no more negligible, and our linear equations cease to be applicable. Therefore, having purposely retained only the first powers of these ratios, we shall have to assume throughout that $R > R_c$. (The question as to what happens below R_c may occupy our attention at a future opportunity.)

Using the critical distance as given above, we can conveniently write

$$\gamma' = \gamma_0 \left[1 - \left(\frac{R_c}{R} \right)^3 \right],$$

or in terms of wave-lengths, remembering that $\gamma = \left(\frac{2\pi c}{\lambda} \right)^2$,

$$\frac{1}{\lambda'^2} = \frac{1}{\lambda_0^2} \left[1 - \left(\frac{R_c}{R} \right)^3 \right], \quad . \quad . \quad . \quad (31)$$

and

$$R_c^3 = \frac{B\lambda_0^2}{2\pi^2 c^2} = \frac{\lambda_0^2}{2\pi^2} \cdot \frac{e^2/c^2}{m}, \quad . \quad . \quad . \quad (32)$$

c being the velocity of light in empty space. The reader will remember that, e being a charge in the electrostatic system, $e^2/c^2 m$ is a certain length. The critical distance is, so to say, the natural unit of interatomic distance. If R contains many of these units, λ' sensibly coincides with λ_0 , giving a close doublet. When R decreases, λ' is lengthened, at first very slowly, but then, when R approaches the natural unit, very rapidly, so that in certain cases the minutest approach of the atoms may suffice to change entirely the "colour" of the resulting substance. To illustrate the increasing rapidity of this process, let us assume λ_0 in the remote ultraviolet, say,

$$\lambda_0 = 720 \text{ \AA.U.},$$

a figure which would closely correspond to the free frequency

* R_c will not be confounded with the "singular distance" $R' = R'(\gamma)$. The latter, a function of γ , is that distance R for which the incident γ becomes identical with γ' . On the other hand, R_c is a constant, whose value depends only on B and γ_0 .

of diamond *, and therefore, possibly, to that of the isolated carbon atom. If this is taken for λ_0 , then, no matter what length R_c is itself, formula (31) gives the following interesting table :—

| | | | | | | | | | | | |
|------------------|-----|-----|-----|------|------|------|-------|-------|-------|--------|----------|
| $R/R_c = \infty$ | 5 | 2 | 1.5 | 1.2 | 1.10 | 1.05 | 1.010 | 1.005 | 1.002 | 1.001 | 1 |
| $\lambda' = 720$ | 723 | 770 | 858 | 1109 | 1444 | 1951 | 4199 | 5908 | 9318 | 13,159 | ∞ |

For $R = 1.5R_c$ the line λ' becomes accessible to the vacuum spectrograph, and for 1.05 for the ordinary quartz spectrograph; when R is just above $1.010R_c$ the visible region of the spectrum is reached, and before it falls to $1.002R_c$, λ' plunges into the infra-red.

With regard to the absolute length of the critical distance itself, it could be determined with precision, if the *true atomic dispersive curve* and therefore λ_0 and B were known, quite apart from the electrical significance of B . We may return later to this aspect of the question. Here, however, let us remark that if the second form of (32) is used, R_c can be put into an interesting form. In fact, if the mass m of the dispersive particle (not necessarily an electron) is of purely electromagnetic origin, and if, to fix the ideas, the charge is assumed to be uniformly distributed through its volume, a sphere of radius a , then

$$m = \frac{e^2/c^2}{5\pi a},$$

and the above expression of the critical distance becomes

$$R_c = \left(\frac{5\lambda_0^2 a}{2\pi} \right)^{1/3} \cdot \cdot \cdot \cdot \cdot \quad (33)$$

* In fact, I find that Martens's observations of the refractive index μ of diamond (Land.-Börn., 1905, p. 631) extending over $\lambda = .313$ to .643 micr., can be fairly well represented by

$$N \equiv \frac{\mu^2 - 1}{\mu^2 + 2} \cdot \frac{M}{d} = \frac{2.078 \lambda^2}{\lambda^2 - \lambda_0^2}, \text{ with } \lambda_0 = 719.9 \text{ \AA.U.} \quad \cdot \cdot \cdot \cdot \cdot \quad (C)$$

Having determined the two constants from μ_{313} and μ_{441} , I obtain from (C)

| | | | | |
|----------------------------|----------|----------|----------|----------|
| $(\lambda = .313)$ | $(.346)$ | $(.441)$ | $(.508)$ | $(.643)$ |
| $N_{\text{calc.}} = 2.195$ | 2.172 | 2.135 | 2.121 | 2.105, |

and, from Martens's observations,

| | | | | |
|---------------------------|-------|-------|-------|--------|
| $N_{\text{obs.}} = 2.195$ | 2.172 | 2.135 | 2.122 | 2.106. |
|---------------------------|-------|-------|-------|--------|

The agreement is, for the present purpose, more than sufficient.

If our dispersive particle is an electron in the proper sense of the word, then a is about $1.8 \cdot 10^{-13}$ cm., and

$$R_c = 5.23 \cdot 10^{-5} \cdot \lambda_0^{2/3}.$$

Thus, for instance, if $\lambda_0 = 1000$ Å.U., then

$$R_c = 2.43 \text{ Å.U.}$$

Thus far the diatomic molecule composed of two *equal* atoms.

More generally we have, for two different atoms, by (18), and replacing again γ by $\left(\frac{2\pi c}{\lambda}\right)^2$,

$$\frac{1}{\lambda'^2} = \frac{1}{2} \left(\frac{1}{\lambda_1^2} + \frac{1}{\lambda_2^2} \right) - \frac{1}{2} \sqrt{\left(\frac{1}{\lambda_1^2} - \frac{1}{\lambda_2^2} \right)^2 + \frac{B_1 B_2}{\pi^4 c^4 R^6}},$$

and a similar expression for λ'' , with $+$ before the radical; but this second "new" wave-length need not detain us since it falls into the remote ultraviolet, if λ_1, λ_2 do so. Here again, the critical distance, marking the limit of stability, is determined by equalling to zero the right member. Thus,

$$\frac{1}{\lambda'^2} = \frac{1}{2} \left(\frac{1}{\lambda_1^2} + \frac{1}{\lambda_2^2} \right) - \frac{1}{2} \sqrt{\left(\frac{1}{\lambda_1^2} - \frac{1}{\lambda_2^2} \right)^2 + \frac{4}{\lambda_1^2 \lambda_2^2} \left(\frac{R_c}{R} \right)^6}, \quad (34)$$

and the critical distance is given by

$$R_c^3 = \frac{\lambda_1 \lambda_2}{2\pi^2 c^2} \sqrt{B_1 B_2}, \quad . \quad . \quad . \quad . \quad (35)$$

differing from (32) only inasmuch as λ_0 and B are replaced by the geometrical means of the free wave-lengths of the atoms and of their coefficients B_1 and B_2 . The discussion of (34), (35), and the illustration of these formulæ by numerical examples, may be left to the reader. No matter how remotely ultraviolet the atomic free oscillations λ_1, λ_2 , the new free oscillations (λ') may well fall into the visible or even the infra-red region, provided that R is but little above the critical distance. Against the opinion, current in more recent times, the infra-red free periods, such as are observed in rock-salt, may well be ascribed to the dispersive electrons under interatomic influence, instead of being attributed to the molecule as a whole or to aggregates of molecules.

Broadening of Absorption Bands.—We have assumed from the beginning that the distances between the atoms, or rather between the centres O_1 , O_2 , etc., are fixed. Our differential equations, however, will continue to be approximately valid if these distances are slightly oscillating between certain extreme values, in other words *, if the R 's are considered as (comparatively) *slowly variable parameters*. To fix the ideas, let us suppose that the "friction," to be taken account of in the equations of motion of the dispersive particles in the neighbourhood of the free periods, is very small. Then, if the distance R were rigorously constant, the corresponding absorption bands, at λ_1 , λ_2 as well as at λ' (and λ''), would be very sharp "lines." If, however, the distance oscillates between R and $R + \delta R$, then the new absorption line will oscillate between λ' and $\lambda' + \delta \lambda'$, and will appear, therefore, as a band of breadth $\delta \lambda'$. In the simplest case of two equal atoms this breadth will be, by (31), and assuming δR to be a small fraction of R ,

$$\delta \lambda' = -\frac{3}{2} \frac{\lambda'^3 R_c^3}{\lambda_0^2 R^4} \delta R,$$

and if R differs but little from R_c ,

$$\delta \lambda' = -\frac{3}{2} \frac{\lambda'^3}{\lambda_0^2} \cdot \frac{\delta R}{R_c}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (36)$$

that is, proportional to the cube of λ' itself. Thus *the broadening of the absorption band due to oscillations of R would be much greater in the red than in the violet region*. This seems to harmonize with general experience. Of course, the bands would, independently of these oscillations, become broader and less sharp with increasing "friction" or "extinction," which, according to Lorentz, is due chiefly to the collisions of the molecules. It is well known that the extinction due to radiation or re-emission of energy alone has been found much too small to account for the absorption phenomena that are actually observed in many cases. It is for this reason that Lorentz ('Theory of Electrons,' pp. 141–142) has taken account of the collisions of molecules. But, as Lorentz himself admits, the collisions, say, in gaseous bodies, are not sufficiently frequent to explain the observed breadth of the absorption bands. Under

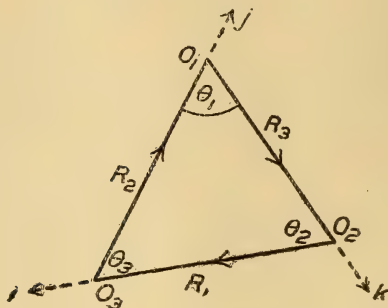
* And without entering into the dynamics of the centres as mass-points.

these circumstances the above result seems to acquire an additional interest, inasmuch as it would account at least for *the breadth* of the bands, if not for the large total amount of absorption. In fact, according to (36) we can have almost any breadth due to δR alone, *i. e.* without taking account at all of the collisions of molecules. Thus, if, in round figures, $\lambda_0 = 1000$ and $\lambda' = 2000 \text{ \AA.U.}$ (that is, by the little table on p. 117, if $R/R_c \doteq 1.10$), then we should have, for $\delta R = -\frac{1}{10}R_c$, $\delta\lambda' = 1200 \text{ \AA.U.}$, *i. e.* what would be called a "general absorption" from 2000 to 3200 \AA.U. , and even for $\delta R = -\frac{1}{1000}R_c$ a rather broad band, stretching over 12 \AA.U. The "general absorption" in the former case would, of course, be a "weak" one, such as are observed in the fatty alcohols.

5. Triatomic Molecules.

Let the three centres O_1, O_2, O_3 , *i. e.* the equilibrium positions of the dispersive particles within their atoms, form any (fixed) triangle. Let R_1, R_2, R_3 be the sides of this triangle, O_2O_3, O_3O_1, O_1O_2 , respectively, and $\theta_1, \theta_2, \theta_3$ its angles (fig. 2). It will be most convenient to write the

Fig. 2.



equations of motion in terms of the components of the displacements r_i taken normally to the molecular plane $O_1O_2O_3$ and along the two sides meeting in O_i . The normal components will be free from interatomic action, and need, therefore, no further attention. If N_1, N_2, N_3 are the three atomic refractivities, and if the planes of the molecules are all parallel to one another, then the *normal*

refractivity $N_n = \omega_n / \alpha \mathfrak{N}$ will be simply

$$N_n = N_1 + N_2 + N_3, \quad . \quad . \quad . \quad . \quad (37)$$

where $N_i = B_i / \alpha (\gamma_i - \gamma)$, as before. The problem, therefore, is reduced to finding the refractivity-operator $N_p = \omega_p / \alpha \mathfrak{N}$ for directions of \mathbf{E} parallel to the molecular planes. The molecular refractivity of an isotropic substance will then easily be found by averaging.

Let $\mathbf{i}, \mathbf{j}, \mathbf{k}$ be three unit vectors directed from O_2 to O_3 , from O_3 to O_1 , and from O_1 to O_2 respectively. Then

$$\mathbf{r}_1 = r_{12}\mathbf{j} + r_{13}\mathbf{k},$$

and similarly for $\mathbf{r}_2, \mathbf{r}_3$. The equations of motion (9) for the six displacement components

$$r_{12}, r_{13}; r_{23}, r_{21}; r_{31}, r_{32}$$

will most conveniently be written in the Lagrangian form

$$\left. \begin{aligned} \frac{d}{dt} \left(\frac{\partial L}{\partial \dot{r}_{23}} \right) + \frac{\partial \Phi}{\partial r_{23}} &= m_2 G_{23}, \text{ etc.} \\ \frac{d}{dt} \left(\frac{\partial L}{\partial \dot{r}_{32}} \right) + \frac{\partial \Phi}{\partial r_{32}} &= m_3 G_{32}, \text{ etc.} \end{aligned} \right\}, \quad . \quad . \quad (38)$$

where $m_2 G_{23}, m_3 G_{32}$ are the generalized forces on r_{23}, r_{32} , due to the external electric field \mathbf{E} , determined by the right-hand members of (9), and where "etc." means always two more equations obtained by cyclic permutations of the suffixes 1, 2, 3. The symbols L and Φ are used for the relevant kinetic and potential energy of the molecular system. These latter functions are easily obtained. Using the abbreviations

$$\rho_i = \frac{2B_i}{R_i^3}, \quad a_i = \cos \theta_i, \quad i=1, 2, 3, \quad . \quad . \quad . \quad (39)$$

we have

$$\left. \begin{aligned} L &= \frac{m_1}{2} (\dot{r}_{12}^2 + \dot{r}_{13}^2 - 2a_1 \dot{r}_{12} \dot{r}_{13}) + \text{etc.}, \\ \Phi &= m_1 \left[\frac{\gamma_1}{2} (r_{12}^2 + r_{13}^2 - 2a_1 r_{12} r_{13}) - \rho_1 r_{21} r_{31} \right] + \text{etc.} \end{aligned} \right\}. \quad (40)$$

Thus the six equations of motion, (38), become

$$\ddot{r}_{23} - a_2 \ddot{r}_{21} + \gamma_2 (r_{23} - a_2 r_{21}) - \frac{m_3}{m_2} \rho_3 r_{13} = G_{23}, \text{ etc.}$$

$$\ddot{r}_{32} - a_3 \ddot{r}_{31} + \gamma_3 (r_{32} - a_3 r_{31}) - \frac{m_2}{m_3} \rho_2 r_{12} = G_{32}, \text{ etc.,}$$

where G_{23} , etc. are homogeneous linear functions of the components of \mathbf{E} , the electric vector in the incident wave. Therefore, for monochromatic light of frequency $n = \sqrt{\gamma}$,

$$\left. \begin{aligned} (\gamma_2 - \gamma) (r_{23} - a_2 r_{21}) - \frac{m_3}{m_2} \rho_3 r_{13} &= G_{23}, \text{ etc.} \\ (\gamma_3 - \gamma) (r_{32} - a_3 r_{31}) - \frac{m_2}{m_3} \rho_2 r_{12} &= G_{32}, \text{ etc.} \end{aligned} \right\} \dots (41)$$

These are six linear equations for the six displacement components r_{23} , etc. Resolving them and substituting r_{23} , etc., as linear functions of the components of \mathbf{E} , into the right-hand member of equation (10) projected upon the molecular plane, we shall have K_p (and therefore also ω_p and N_p) as a linear vector operator in that plane. Since $\frac{1}{2} \mathbf{E}_p K_p \mathbf{E}_p$ has to represent the (density of) electric energy, K_p , and therefore N_p , should be self-conjugate operators. Thus N_p will have, in the molecular plane, two orthogonal principal axes, and two principal values, say, N_{p1} and N_{p2} , generally differing from one another. Now, the determinant of the system (41) is of the *sixth* degree in γ . The roots, γ' , etc., of that determinant equalled to zero will be the squared *free frequencies* of the molecule, produced by atomic interaction. Whatever the shape of the molecule, *i. e.* of the triangle $O_1 O_2 O_3$, all of these roots will be real and positive, provided that the inter-atomic distances R_i do not fall below certain values marking the limit of optical stability*. Thus, within the range of stability, there will be six real free frequencies, in general different from one another, belonging to the oscillations in the molecular plane, besides the three original atomic ones, which belong to oscillations normal to that plane. These will be shortly referred to as the *normal* oscillations and frequencies.

In the case of equal orientation of all molecules, therefore, the resulting substance will be a *pleochroistic crystal with*

* In other words, Φ , in (40), will be a positive quadratic form, provided that ρ_1, ρ_2, ρ_3 are small enough.

three electrical, i. e. with two optical axes; of its three principal molecular refractivities, N_n , N_{p_1} , N_{p_2} , the first only will obey the additive law and show the original absorption bands γ_1 , γ_2 , γ_3 as in (37), while the remaining two, showing six new absorption bands, will contain products of the atomic refractivities and will depend upon the size and the shape of the molecule, i. e. upon the R 's and θ 's. Each of these latter refractivities will, in general, be of the form $f'_5(\gamma)/\text{Det.}$, where f'_5 is of the 5th degree in γ and Det. the determinant of (41); that is,

$$N_{p_1} = \frac{A'}{\gamma' - \gamma} + \dots + \frac{A^{iv}}{\gamma^{vi} - \gamma},$$

and similarly for N_{p_2} , where the coefficients A' , etc., will depend upon the intrinsic attributes, as well as upon the configuration, of the three atoms.

And in the case of haphazardly distributed orientations of the molecules we shall have an *isotropic substance* whose molecular refractivity,

$$N = \frac{1}{3}(N_n + N_{p_1} + N_{p_2}), \quad . \quad . \quad . \quad (42)$$

will differ from the sum of the atomic refractivities in a manner depending upon the size and the shape of the molecules. Its dispersion formula will, in general, consist of nine terms, corresponding to as many free frequencies or absorption bands, three due to the atoms themselves, and six due to their interaction. The formula for N as a function of γ , similar to (16), with $\omega/\mathfrak{N} = \alpha N$, will be, in the general case of unequal roots of $\text{Det} = 0$,

$$N = \frac{1}{3\alpha} \sum_1^3 \frac{B_i}{\gamma_i - \gamma} + \frac{1}{3\alpha} \sum_1^6 \frac{B^{(i)}}{\gamma^{(i)} - \gamma}, \quad . \quad . \quad (43)$$

where $\gamma^{(i)}$ are the six new frequencies, $B_i = e_i^2/m_i$, and $B^{(i)}$, i. e. B' , B'' , etc., are six coefficients depending upon the attributes of the three atoms and upon their configuration within the molecule. The new (squared) frequencies $\gamma^{(i)}$, that is γ' , γ'' , etc., will also be functions of the configuration, and of the old frequencies. If two roots coincide, say $\gamma' = \gamma''$, then we shall have, in the dispersion formula,

a term of the form $\frac{\text{const.}}{(\gamma' - \gamma)^2}$ besides $\frac{\text{const.}}{\gamma' - \gamma}$, and so on.

For the present it will be enough to develop our general formulæ, and especially to find the new frequencies, in the

simplest case of *equal atoms, forming an equilateral triangle*, or of what may be called a *regular triatomic molecule*. Such would be the molecules of ozone. The case of any isosceles triangle (with the limiting case of collinear atoms), which would correspond to water or to the important group CH_2 , may be left to the reader.

Regular Triatomic Molecule.—In this case we have

$$a_1 = a_2 = a_3 = \frac{1}{2},$$

further,

$$R_i = R, \quad \gamma_i = \gamma_0, \quad B_i = B = e^2/m,$$

and, finally,

$$\rho_i = \rho = 2B/R^3.$$

Thus the system of six equations (41) becomes, with a convenient rearrangement of their order,

$$\left. \begin{aligned} r_{23} - g(r_{13} - \frac{1}{2}r_{12}) &= -\frac{1}{\rho}G_{13}, \text{ etc.} \\ r_{32} - g(r_{12} - \frac{1}{2}r_{13}) &= -\frac{1}{\rho}G_{12}, \text{ etc.} \end{aligned} \right\}, \quad \dots \quad (44)$$

where G_{23} , etc. are homogeneous linear functions of the components of \mathbf{E} , as defined above, and g is an abbreviation for $(\gamma_0 - \gamma)/\rho$, so that

$$\gamma = \gamma_0 - \rho g = \gamma_0 - \frac{2B}{R^3}g. \quad \dots \quad (45)$$

Let us consider the first line of (44) as the 1st, 2nd, and 3rd equations, and the second line as the 4th, 5th, and 6th equations. Let this be the order of the rows, and let the columns correspond to r_{23} , r_{31} , r_{12} , r_{32} , r_{13} , r_{21} . Then the determinant of the system (44) will be

$$D = \begin{vmatrix} 1 & 0 & g/2 & 0 & -g & 0 \\ g/2 & 1 & 0 & 0 & 0 & -g \\ 0 & g/2 & 1 & -g & 0 & 0 \\ 0 & 0 & -g & 1 & g/2 & 0 \\ -g & 0 & 0 & 0 & 1 & g/2 \\ 0 & -g & 0 & g/2 & 0 & 1 \end{vmatrix}, \quad \dots \quad (46)$$

showing a peculiar regularity of structure. Developing it, we obtain

$$D = 1 - 3g^2 + \frac{1}{4}g^3 + \frac{9}{4}g^4 - \frac{27}{64}g^6. \quad . \quad . \quad (46 \ a)$$

The interesting part of our problem consists not so much in constructing the coefficients $B^{(i)}$ of the final dispersion formula (43), as in actually finding the "new" free frequencies, $\sqrt{\gamma'}$, $\sqrt{\gamma''}$, etc. These will belong to the molecule in absence of \mathbf{E} , that is for $G_{13}=0$, etc., when the equations (44) become

$$r_{23} = g(r_{13} - \frac{1}{2}r_{12}), \text{ etc.}; \quad r_{32} = g(r_{12} - \frac{1}{2}r_{13}), \text{ etc.}, \quad . \quad (44 \ o)$$

defining the ratios of the six displacement components in the molecular plane. The required free frequencies will be given by the roots g' , g'' , etc. of the equation $D=0$, where D is as in (46) or (46 a). This is an equation of the *sixth* degree, containing not only g^2 , $(g^2)^2$, $(g^2)^3$, but also g^3 . At first, the task of solving it rigorously seemed hopeless. But the form of (44 o) suggested that it would be worth while to try whether these equations can be satisfied by assuming

$$r_{12} = r_{23} = r_{31} = x, \text{ say,}$$

and

$$r_{21} = r_{32} = r_{13} = y.$$

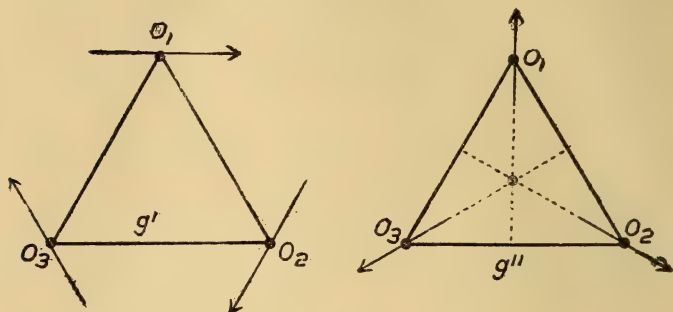
This has turned out to be the case. In fact, on substitution in (44 o) we find that these six equations are all satisfied, provided that $x/y = (1 + \frac{1}{2}g) : g = g : (1 + \frac{1}{2}g)$, and therefore, $g^2 - \frac{4}{3}g = \frac{4}{3}$, that is to say, either

$$\text{or} \quad \left. \begin{array}{l} g = g' = 2, \quad \text{and} \quad y = x \\ g = g'' = -\frac{2}{3}, \quad \text{and} \quad y = -x \end{array} \right\} . \quad . \quad . \quad . \quad (47)$$

This gives at once two roots of $D=0$. The first of these might have also been derived directly from the tabular form (46). In fact, $1 - \frac{1}{2}g$ is the sum of the elements of each row (or of each column) of that determinant, and therefore a factor of D . At any rate, we have in (47) two of the six roots and, at the same time, the corresponding fundamental modes of vibration, which are shown in fig. 3.

In both cases the amplitudes and the phases of \mathbf{r}_1 , \mathbf{r}_2 , \mathbf{r}_3 are equal; in the first case each of the three dispersive particles oscillates parallel to the opposite side, and in the second, along the straight line joining its position of equilibrium with the centre of the triangle $O_1O_2O_3$.

Fig. 3.



Both roots are verified on actually dividing (46 a) by the corresponding factors, which gives the identity

$$D \equiv (1 - \frac{1}{2}g) (1 + \frac{3}{2}g) \cdot (1 - g - \frac{5}{4}g^2 + \frac{3}{4}g^3 + \frac{9}{16}g^4).$$

Thus our sextic is reduced to the quartic equation

$$g^4 + \frac{4}{3}g^3 - \frac{20}{9}g^2 - \frac{16}{9}(g-1) = 0,$$

which is easily solved. In fact, applying Euler's method, we find that it has the *two equal* roots $\frac{-1 - \sqrt{13}}{3}$ and the *two equal* roots $\frac{-1 + \sqrt{13}}{3}$.

Together with those given in (47) we have, therefore, all the six roots of $D=0$,

$$\left. \begin{aligned} g' &= 2; \quad g'' = -\frac{2}{3}; \quad g''' = -\frac{\sqrt{13}+1}{3} \text{ (double); } \\ g^{iv} &= \frac{\sqrt{13}-1}{3} \text{ (double), } \end{aligned} \right\} \quad (48)$$

and the identity, which may be useful at a future opportunity,

$$D \equiv -(\frac{3}{4})^3 \cdot (g-g') (g-g'') (g-g''')^2 (g-g^{iv})^2. \quad (49)$$

Returning to our chief subject, we have for the squared frequencies of the *free vibrations in the molecular plane*, by (48) and (45),

$$\left. \begin{aligned} \gamma' &= \gamma_0 - \frac{4B}{R^3}, & \gamma'' &= \gamma_0 + \frac{4}{3} \frac{B}{R^3}, \\ \gamma''' &= \gamma_0 + \frac{2}{3}(1 + \sqrt{13}) \frac{B}{R^3} \text{ (double)}, \\ \gamma^{iv} &= \gamma_0 - \frac{2}{3}(\sqrt{13} - 1) \frac{B}{R^3} \text{ (double)}, \end{aligned} \right\} \quad . \quad . \quad (50)$$

besides the “normal” free frequency, $\sqrt{\gamma_0}$, which belongs to each of the atoms. In all, therefore, we have *five different free frequencies*, of which two are “double”*. Thus, a substance composed of regular triatomic molecules would show *five distinct absorption bands*, or, speaking rigorously, seven bands, of which four would coincide in pairs.

Notice in passing that, by (50), the sum of the squares of the six new frequencies in the molecular plane is again equal to that of the old ones, *i. e.*

$$\gamma' + \gamma'' + 2\gamma''' + 2\gamma^{iv} = 6\gamma_0,$$

as might have been expected.

Let γ_0 be in the remote ultraviolet. Then γ'' and γ''' will be still more remote, and therefore inaccessible. But the remaining two absorption bands, γ' and γ^{iv} , will always be more accessible than γ_0 , and may well fall into the visible or even the infra-red region of the spectrum, provided that the size of the molecule, *i. e.* the distance R between its atoms, is small enough.

The longest wave corresponds, by (50), to the new frequency $\sqrt{\gamma'}$. As long as this is real, all others are real. Thus, the critical distance $R = R_c$, marking the limit of absolute optical stability, will, in the present case, be given by

$$R_c^3 = \frac{4B}{\gamma_0}$$

or, in terms of λ_0 ,

$$R_c^3 = \frac{\lambda_0^2 B}{\pi^2 c^2} = \frac{\lambda_0^2}{\pi^2} \cdot \frac{e^2/c^2}{m}, \quad . \quad . \quad . \quad (51)$$

* And as such would be split by a magnetic field into doublets (inverse Zeeman-effect): But this by the way only.

and if the dispersive particles are pure spherical charges, of radius a ,

$$R_c^3 = \frac{5}{\pi} \lambda_0^2 a, \quad . \quad . \quad . \quad . \quad . \quad (51a)$$

as in the case of diatomic molecules, (33), the only difference being that $\frac{5}{2}$ is now replaced by 5. In short, the critical distance for a regular triatomic molecule is 1.260 times that for a diatomic molecule, composed of the same atoms.

The two infra- λ_0 absorption bands can now be written

$$\frac{1}{\lambda'^2} = \frac{1}{\lambda_0^2} \left[1 - \frac{R_c^3}{R^3} \right]; \quad \frac{1}{\lambda^{iv2}} = \frac{1}{\lambda_0^2} \left[1 - 0.434 \frac{R_c^3}{R^3} \right]. \quad (52)$$

When R approaches R_c (from above), the wave-length λ' tends to disappear in the remote infra-red, while λ^{iv} , moving more lazily, tends to become only 1.329 times λ_0 . Thus, for example, if $\lambda_0 = 720 \text{ \AA.U.}$, the greatest length of λ^{iv} , compatible with stability, is 957 \AA.U. , still in the extreme Lyman-region. But λ' may fall into any region of the spectrum, from λ_0 to infinity,—precisely as our previous λ' in the case of a diatomic molecule.

This settles the question of the free frequencies belonging to a regular triatomic molecule. The refractivity of a substance composed of such molecules, as a function of the frequency $\sqrt{\gamma}$ of the incident light, will contain seven terms having in their denominators the expressions

$$\gamma_0 - \gamma, \quad \gamma' - \gamma, \quad \gamma'' - \gamma, \quad (\gamma''' - \gamma)^2, \quad \gamma''' - \gamma, \quad (\gamma^{iv} - \gamma)^2, \quad \gamma^{iv} - \gamma.$$

The corresponding coefficients, as functions of the attributes of the atoms and of their mutual distances, will be determined by means of (44) and (10). Further details concerning triatomic and some of the more complex molecules will be given in a later publication.

I gladly take the opportunity of thanking my friend Dr. A. G. Goldsobel for having directed my attention to this subject and for furnishing many interesting chemical data.

November 14, 1916.

VIII. *The Scattering and the Absorption of the Gamma Rays.*
 By M. ISHINO, *Rigakushi (Kyoto Imperial University, Japan), Research Student of Victoria University of Manchester* *.

CONTENTS.

- § 1. Introductory.
- § 2. Principle of the Method for the Determinations of the Scattering-coefficient and the true Absorption-coefficient.
- § 3. Experimental Details.
- § 4. Results.
- § 5. Conclusions.

§ 1. *Introductory.*

IT is well known that the gamma rays are scattered in their passage through matter. The nature of the scattered rays has been studied by Kleeman †, Madsen ‡, Florance §, and Gray ||. Florance made a careful investigation of the amount of scattering in different directions with the incident beam, and drew attention to the variation in penetrating power of the radiation scattered in different directions.

Measurements of the absorption coefficient of gamma rays from radium in passing through matter have been made by a number of investigators, including Sir E. Rutherford ¶, McClelland **, Eve ††, Wiegger ‡‡, Tuomikoski §§, Soddy and Russell |||, Florance ¶¶, Oba ***, and Mr. & Mrs. Soddy and Russell †††. The values of the absorption coefficients, obtained by the ordinary methods, show considerable variation depending upon the conditions of measurement.

* Communicated by Sir E. Rutherford, F.R.S.

† Kleeman, *Phil. Mag.* xv. p. 638 (1908).

‡ Madsen, *Phil. Mag.* xvii. p. 423 (1909).

§ Florance, *Phil. Mag.* xx. p. 921 (1910); xxvii. p. 225 (1914).

|| Gray, *Phil. Mag.* xxvi. p. 611 (1913).

¶ Sir E. Rutherford, *Phys. Zeit.* iii. p. 517 (1902).

** McClelland, *Phil. Mag.* viii. p. 67 (1904).

†† Eve, *Phil. Mag.* xvi. p. 224 (1908); xviii. p. 275 (1909).

‡‡ Wiegger, *Jahr. Radioakt.* ii. p. 430 (1905).

§§ Tuomikoski, *Phys. Zeit.* x. p. 372 (1909).

||| Soddy and Russell, *Phil. Mag.* xviii. p. 620 (1909).

¶¶ Florance, *Phil. Mag.* xxvii. p. 225 (1914).

*** Oba, *Phil. Mag.* xxvii. p. 601 (1914).

††† Mr. & Mrs. Soddy and Russell, *Phil. Mag.* xix. p. 725 (1910).

For instance, the value of the coefficient depends to some extent upon the thickness of the absorbing materials, and also on the relative position of the absorber with respect to the source of gamma rays and the testing vessel. The discrepancies are generally ascribed to the different amount of scattered rays which enter the testing vessel under the experimental conditions. The loss of intensity of a primary beam of gamma rays in its passage through an absorbing material, under the condition that the scattered rays are completely prevented from entering the testing vessel, can be conveniently divided into two parts. One part results from a true absorption of the rays in the material where the energy of the rays is transformed into energy of a different form. The other part is due to a true scattering of the primary beam. Let μ and σ be the coefficients of the true absorption and of the true scattering respectively. Suppose a fine beam of homogeneous gamma rays penetrate into a plate normally to its surface. Let the intensity of the beam at any point in the plate, distant x from the incident surface, be I ; then the change of the intensity dI in the distance dx should be the sum of $-\mu I dx$ due to true absorption and $-\sigma I dx$ due to scattering: *i. e.*,

$$dI = -I(\mu + \sigma)dx.$$

Hence we have, for the intensity of the emergent beam,

$$I = I_0 e^{-(\mu + \sigma)t}, \quad . \quad . \quad . \quad . \quad (1)$$

where I_0 is the initial intensity of the beam, and t the thickness of the plate. Consequently, the coefficient of the loss of energy is the sum of the coefficients of true absorption and of true scattering. In the case where a part of the scattered rays enters the testing vessel, the coefficient of the loss of energy should give a value intermediate between μ and $\mu + \sigma$, and this value is usually taken as the coefficient of absorption. It is for this reason that the observed values of the absorption coefficients found by different observers show divergences often greater than the experimental error.

The present researches were undertaken to determine the two coefficients μ and σ separately, and to find the relation between σ and the scattering materials.

During the course of the present experiments a paper has been published by Hull and Marion Rice* on the law of

* Hull and Marion Rice, *Phys. Review*, viii. p. 326 (1916).

absorption of X rays of high frequencies, using a Coolidge tube as a source of radiation. Under the experimental conditions, where the scattered rays did not enter the testing vessel, they found that the apparent mass absorption coefficient λ/ρ was given by an equation of the following form :—

$$\frac{\lambda}{\rho} = \frac{\mu}{\rho} + \frac{\sigma}{\rho}.$$

They assumed that μ/ρ , or the “mass transformation coefficient,” was proportional to the cube of the wave-length of the X ray, and that σ/ρ was a universal constant, independent of the wave-length of the ray and of the material ; so that

$$\frac{\lambda}{\rho} = al^3 + b,$$

where l is the wave-length. From Barkla's data, b was taken as 0.12. They showed that the values of λ in aluminium and copper, which they measured, satisfied approximately the following equations :

$$\left(\frac{\lambda}{\rho}\right)_{\text{Al}} = 14.9 l^3 + 0.12,$$

and

$$\left(\frac{\lambda}{\rho}\right)_{\text{Cu}} = 150 l^3 + 0.12,$$

respectively, where l was in Å.U. They found that the absorption of X rays in lead was complicated by the appearance of a marked absorption band, which appeared when the wave-length was 0.149 Å.U. For the lowest wave-length examined, viz. 0.122, the value of λ/ρ was 3.00 for lead.

The wave-lengths of the penetrating gamma rays from radium have been experimentally determined by Sir E. Rutherford and Andrade*. The two shortest wave-lengths observed in their experiments were .071 and .099 Å.U. Since the value of λ/ρ found in this present paper is about .076, *i. e.* about $\frac{1}{40}$ of the value found by Hull and Rice for $\lambda=0.122$, it seems probable that the penetrating gamma rays from radium C contain waves of much shorter length than those observed experimentally†. Hull and

* Sir E. Rutherford and Andrade, *Phil. Mag.* xxviii. p. 263 (1914).

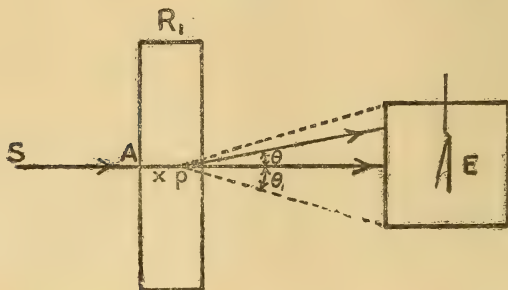
† See Sir E. Rutherford's British Association Address, ‘Engineering,’ Oct. 6, 1916.

Rice expressly point out that their equation connecting wave-length and absorption cannot be extrapolated for lead beyond the wave-lengths examined by them. It is obvious that this is the case not only for lead but for other elements, since the values of λ/ρ found in this present paper for aluminium and lead, viz. .071 and .076 respectively, in the case of the penetrating gamma rays, are considerably less than the value of 0.12 taken by Hull and Rice for the scattering coefficient alone. Such results indicate that the scattering coefficient decreases in value for high frequencies, and that the formulæ given by Hull and Rice cannot be extrapolated.

§ 2. *Principle of the Method for the Determination* of the Scattering Coefficient and the True Absorption Coefficient.*

Suppose a very narrow beam SA of homogeneous gamma rays penetrates a plate R_1 normal to its surface (fig. 1).

Fig. 1.



The intensity I of the beam at a point P in the plate distant x from the incident surface is, by (1),

$$I = I_0 e^{-(\mu + \sigma)x}.$$

The primary beam is scattered in all directions under some law of distribution. Let us denote this law by $f(\theta)$, where θ is the angle measured from the direction of the primary beam. Then the amount of scattered rays proceeding from P in a hollow cone of semi-angle θ and thickness $d\theta$ is

$$I_0 e^{-(\mu + \sigma)x} \sigma f(\theta) e^{-(\mu + \sigma)(t-x) \sec \theta} 2\pi \sin \theta \cdot d\theta \cdot dx.$$

The total amount, S_1 , of the scattered rays which enter the electroscope E, therefore, is

$$S_1 = 2\pi I_0 \sigma e^{-(\mu+\sigma)t} \int_0^t \int_0^{\theta_1} e^{(\mu+\sigma)x(\sec\theta-1)} f(\theta) \sin\theta d\theta dx, \quad (2)$$

where t is the thickness of the plate and θ_1 is half the angle subtended at the point P by the side of the electroscope E. The intensity, I_1 , of the beam which reaches the electroscope is

$$I_1 = I_0 e^{-(\mu+\sigma)t} + S_1. \quad (3)$$

If the plate be close to the electroscope then the upper limit of the integral with respect to θ in (2) is approximately $\pi/2$, and therefore the amount, S_2 , of the scattered rays entering the electroscope in this case is

$$S_2 = 2\pi I_0 \sigma e^{-(\mu+\sigma)t} \int_0^t \int_0^{\pi/2} e^{(\mu+\sigma)x(\sec\theta-1)} f(\theta) \sin\theta d\theta dx, \quad (4)$$

which is the total amount of the emergent scattered rays. The total intensity, I_2 , of the beam which reaches the electroscope is given by

$$I_2 = I_0 e^{-(\mu+\sigma)t} + S_2. \quad (5)$$

The difference between (3) and (5) is

$$\begin{aligned} I_2 - I_1 &= S_2 - S_1 \\ &= 2\pi I_0 \sigma e^{-(\mu+\sigma)t} \int_0^t \int_{\theta_1}^{\pi/2} e^{(\mu+\sigma)x(\sec\theta-1)} f(\theta) \sin\theta d\theta dx \\ &= S, \text{ say.} \end{aligned} \quad (6)$$

Hence, if this integral can be evaluated, we can find the value of σ from the observed values of S and $(\mu+\sigma)$. Strictly speaking, θ is a function of x ; but if the plate be very thin, θ can be considered to be approximately independent of x , and we have for (6)

$$S = \frac{2\pi I_0 \sigma}{\mu + \sigma} e^{-(\mu+\sigma)t} \int_{\theta_1}^{\pi/2} \frac{e^{(\mu+\sigma)(\sec\theta-1)t} - 1}{\sec\theta - 1} f(\theta) \sin\theta d\theta. \quad (6')$$

To integrate (6') with respect to θ , the expression $f(\theta)$ must be known. According to Sir J. J. Thomson's theory of scattering of X rays, the intensity of scattered radiation in any direction is proportional to $1 + \cos^2\theta$, and may be written

$$I_\theta = I_{\pi/2}(1 + \cos^2\theta).$$

The experiments of Barkla and Ayres *, Owen †, and Crowther ‡, however, showed that this expression was inadequate for X rays. Florance § and Madsen || showed that the distribution of scattered gamma rays was very different from that observed for scattered X rays ; but they did not find any simple expression for the distribution-law. At the present stage the data are not sufficiently definite to evaluate the integral in (6').

In the case where the distance of the plate at R_1 (fig. 2) from the electroscope is very large compared with the linear dimensions of the receiving surface of the electroscope, the amount of the rays scattered by the material entering the electroscope is negligible, and therefore we have approximately

$$I_1 = I_0 e^{-(\mu + \sigma)t}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

in place of (3). If the plate be thin, we may, to a first approximation, neglect the absorption of the scattered rays in the material ; and we may also assume that, when the plate is close to the electroscope, the whole of the emergent scattered rays enter the electroscope.

We have then, in place of (5),

$$I_2 = I_0 e^{-\mu t}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

The equation does not take into account the small fraction of the radiation scattered in the backward direction ; this point will be discussed later. By the formulæ (7) and (8) we can find μ and σ from the observed values of I_0 , I_1 , and I_2 . The deviation of the values of μ and σ so obtained from their true values should decrease as the thickness of the plate is reduced. Therefore such measurements should be made with very thin plates. The experiments with very thin plates, however, did not give concordant results, since very small changes in the sensitiveness of the electroscope and errors of observation have a relatively large effect in deducing the values of μ and σ . It was found, however, that the values for very thin plates could be deduced by extrapolation from observation on thick plates.

* Barkla and Ayres, *Phil. Mag.* xxi. p. 270 (1911).

† Owen, *Proc. Cambr. Phil. Soc.* xvi. p. 161 (1911).

‡ Crowther, *Proc. Roy. Soc. A.* lxxxv. p. 29 (1912).

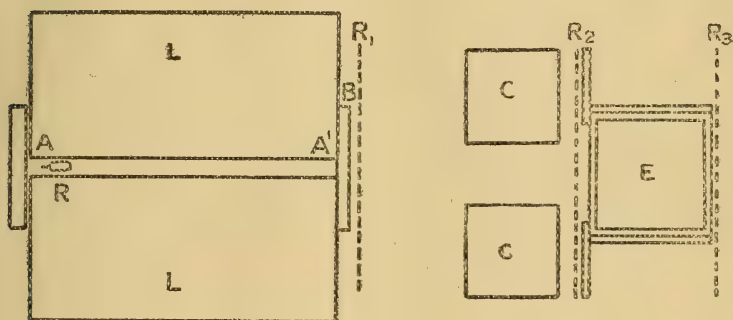
§ Florance, *Phil. Mag.* xx. p. 921 (1910).

|| Madsen, *Phil. Mag.* xvii. p. 423 (1909).

§ 3. Experimental Details.

The general arrangement of the apparatus is shown in fig. 2. Radium-emanation in a closed glass tube was used as the source of gamma rays. The source R was placed near the end A of a cylindrical hole AA', 1.4 cm. in diameter, passing through the centre of a lead cube LL, of 25 cm. side, so that a narrow beam of rays was obtained, of angle of about 2° in most cases.

Fig. 2.



The electroscope E was a cube of 10 cm. side, made of aluminium plate 3.2 mm. thick, and was covered with lead plate 2.5 mm. thick except the two sides through which the beam passed. Glass windows for observing the leaf were protected by lead, in order to exclude secondary β rays. The gold leaf was charged to 400 volts, and the natural leak was .20 to .18 div./min. throughout the experiments. The distance between the electroscope E and the front face N of the lead block LL was 36 cm. To make sure that any stray rays, which might pass outside the hole AA', could not enter the electroscope, and also to cut off the scattered rays from plates at R₁ at wide angles, a thick lead block CC, 7.5 cm. thick, with a hole 5 cm. in diameter, was placed close to the receiving surface of the electroscope. The semi-angle of the cone described by A' as vertex and the hole in CC as the base was not greater than 5° .

From 100 to 150 millicuries of radium emanation were used as a source of gamma rays. The rays were screened

by a lead plate B 1 cm. thick at A', so that the soft gamma rays from radium B and radium C were practically cut off, and the hard rays from radium C only were used. The source, under the above-mentioned experimental arrangement, gave a convenient value of the ionization current, viz. about 10 div./min. in most cases.

Aluminium, lead, and iron plates were used as the absorbers and the radiators. They were all square in shape, 20 cm. in side and of various thicknesses. Mercury was also used. The measurements of the gamma-ray activity through the plates were carried out with the plates in three positions: (1) close to the lead block LL at R₁, (2) close to the front surface of the electroscope at R₂, and (3) close to the back surface of the electroscope at R₃. The readings due to the decaying source alone were taken before and after each series of measurements at R₃, and the intensity of the source corresponding to the moment when the measurements with the plates were performed was found. The observed values of the ionization current, after correcting for the natural leak of the electroscope, were expressed in percentages of the corresponding intensity of the source when the radiator was removed.

§ 4. Results.

The observed results are tabulated in the following tables:—

TABLE I.—Aluminium.

| Thickness of Plate (<i>t</i>). cm. | Mass of Unit Area (ρt). gr.-cm. ⁻² | Ionization Current. | | | Apparent Scattering in forward direction (S). |
|--|---|---------------------|-------------------------|-------------------------|---|
| | | Source alone. | Plate in Position 1. | Plate in Position 2. | |
| ·058 | ·154 | 100·0 | 98·88 | 99·48 | 0·60 |
| ·160 | ·423 | „ | 97·56 | 99·06 | 1·50 |
| ·322 | ·853 | „ | 95·35 | 97·95 | 2·60 |
| ·485 | 1·286 | „ | 93·05 | 96·95 | 3·90 |
| ·644 | 1·717 | „ | 91·25 | 95·95 | 4·70 |
| ·965 | 2·58 | „ | 88·24 | 94·26 | 6·02 |
| 1·33 | 3·45 | „ | 83·62 | 91·81 | 8·19 |
| 1·63 | 4·31 | „ | 80·16 | 89·81 | 9·65 |
| 1·95 | 5·18 | „ | 76·21 | 86·96 | 10·75 |
| 2·28 | 6·05 | „ | 72·26 | 84·55 | 12·29 |
| 2·44 | 6·49 | „ | 69·73 | 82·03 | 12·30 |
| 2·94 | 7·80 | „ | 66·25 | 79·64 | 13·36 |

TABLE II.—Iron.

| Thickness of Plate (<i>t</i>). cm. | Mass of Unit Area (ρt). gr.-cm. ⁻² | Ionization Current. | | | Apparent Scattering in forward direction (S). |
|--|---|---------------------|-------------------------|-------------------------|---|
| | | Source alone. | Plate in Position 1. | Plate in Position 2. | |
| ·0926 | ·727 | 100·0 | 98·17 | 95·87 | 2·30 |
| ·195 | 1·528 | „ | 96·18 | 91·59 | 4·59 |
| ·287 | 2·25 | „ | 94·39 | 88·53 | 5·86 |
| ·388 | 3·04 | „ | 92·41 | 85·09 | 7·32 |
| ·480 | 3·77 | „ | 90·45 | 82·01 | 8·44 |
| ·581 | 4·56 | „ | 88·65 | 78·88 | 9·77 |
| ·673 | 5·28 | „ | 86·73 | 76·10 | 10·63 |
| ·763 | 5·99 | „ | 84·75 | 72·92 | 11·83 |

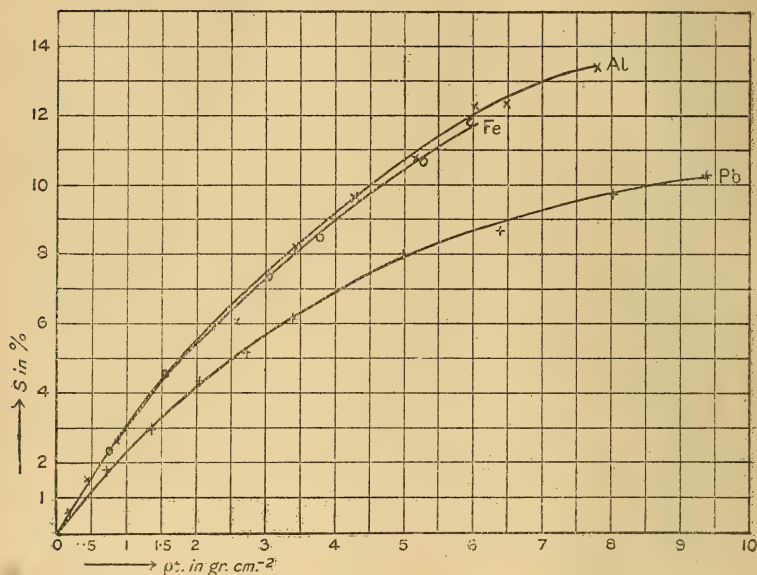
TABLE III.—Lead.

| Thickness of Plate (<i>t</i>). cm. | Mass of Unit Area (ρt). gr.-cm. ⁻² | Ionization Current. | | | Apparent Scattering in forward direction (S). |
|--|---|---------------------|-------------------------|-------------------------|---|
| | | Source alone. | Plate in Position 1. | Plate in Position 2. | |
| ·061 | ·696 | 100·0 | 97·30 | 95·46 | 1·84 |
| ·121 | 1·38 | „ | 91·39 | 94·38 | 2·99 |
| ·180 | 2·04 | „ | 87·79 | 92·13 | 4·34 |
| ·240 | 2·73 | „ | 84·59 | 89·74 | 5·15 |
| ·300 | 3·41 | „ | 81·17 | 87·31 | 6·14 |
| ·441 | 5·01 | „ | 73·60 | 81·65 | 8·0 |
| ·561 | 6·38 | „ | 67·66 | 76·33 | 8·67 |
| ·705 | 8·02 | „ | 61·53 | 71·25 | 9·72 |
| ·825 | 9·38 | „ | 56·74 | 67·01 | 10·27 |

The values *S*, given in the 6th column of the Tables, entitled “apparent scattering in forward direction,” are simply the difference between the values given in the 5th and 4th columns. The theoretical expression for *S* is given by the formula (6) or (6'). These values of the apparent scattering must be smaller than the true values, since the scattered rays were reduced by absorption in escaping from the radiating plate. In fig. 3 the values of *S* are plotted against ρt . It is seen that the curves are not straight lines, but gradually slope towards the axis of ρt . This is an indication that the scattered rays are reduced by absorption. The curve for lead is much lower than those for aluminium and iron; while the curves for the two latter nearly coincide. This point will be discussed later.

The difference between the ionization currents with and without the radiating plate at R_3 behind the electroscope (fig. 2), when corrected for the absorption of the primary beam by the walls of the electroscope, should give the

Fig. 3.



amount of scattering in the backward direction. A number of such observations have been made. It was found, however, that the difference in the readings was too small to be determined with any great accuracy by direct electroscopic method, amounting generally to only a few per cent. Accordingly, only the mean value of the ratios of the scattering in the backward to that in the forward direction was estimated, and found on an average to be 15 per cent. Madsen* estimated the ratio to be about 18 per cent.

By the formula (7) the value of $\mu + \sigma$ was calculated from the figures in the 3rd and 4th columns in the preceding tables; similarly, by the formula (8), the value of μ from the figures in the 3rd and 5th columns. The values so obtained are given in Tables IV. to VI.

* Madsen, Phil. Mag. xvii. p. 423 (1909).

TABLE IV.—Aluminium.

| t . | ρt . | $\mu + \sigma$. | μ . | σ_d . Difference between 3rd and 4th columns. | σ_k . Calculated from formula (9). |
|-------|------------|------------------|---------|--|--|
| ·058 | ·154 | ·194 | ·0895 | ·104 | ·104 |
| ·160 | ·423 | ·155 | ·059 | ·096 | ·096 |
| ·322 | ·853 | ·148 | ·065 | ·083 | ·085 |
| ·485 | 1·286 | ·148 | ·064 | ·084 | ·080 |
| ·644 | 1·717 | ·142 | ·064 | ·078 | ·080 |
| ·965 | 2·58 | ·130 | ·061 | ·069 | ·071 |
| 1·33 | 3·45 | ·134 | ·064 | ·070 | ·074 |
| 1·63 | 4·31 | ·136 | ·066 | ·069 | ·074 |
| 1·95 | 5·18 | ·139 | ·072 | ·067 | ·072 |
| 2·28 | 6·05 | ·144 | ·074 | ·071 | ·075 |
| 2·44 | 6·49 | ·148 | ·081 | ·067 | ·072 |
| 2·94 | 7·80 | ·140 | ·077 | ·062 | ·069 |

TABLE V.—Iron.

| t . | ρt . | $\mu + \sigma$. | μ . | σ_d . Difference between 3rd and 4th columns. | σ_k . Calculated from formula (9). |
|-------|------------|------------------|---------|--|--|
| ·0926 | ·727 | ·456 | ·199 | ·259 | ·260 |
| ·195 | 1·528 | ·447 | ·200 | ·247 | ·257 |
| ·287 | 2·25 | ·422 | ·201 | ·221 | ·244 |
| ·388 | 3·04 | ·405 | ·203 | ·202 | ·222 |
| ·480 | 3·77 | ·413 | ·208 | ·205 | ·214 |
| ·581 | 4·56 | ·407 | ·207 | ·200 | ·223 |
| ·673 | 5·28 | ·405 | ·211 | ·194 | ·208 |
| ·763 | 5·99 | ·401 | ·216 | ·185 | ·213 |

TABLE VI.—Lead.

| t . | ρt . | $\mu + \sigma$. | μ . | σ_d . Difference between 3rd and 4th columns. | σ_k . Calculated from formula (9). |
|-------|------------|------------------|---------|--|--|
| ·061 | ·696 | ·759 | ·449 | ·310 | ·316 |
| ·121 | 1·38 | ·750 | ·481 | ·269 | ·273 |
| ·180 | 2·04 | ·722 | ·455 | ·268 | ·275 |
| ·240 | 2·73 | ·696 | ·454 | ·242 | ·253 |
| ·300 | 3·41 | ·697 | ·453 | ·244 | ·252 |
| ·441 | 5·01 | ·696 | ·460 | ·236 | ·246 |
| ·561 | 6·38 | ·697 | ·482 | ·215 | ·228 |
| ·705 | 8·02 | ·689 | ·481 | ·208 | ·224 |
| ·825 | 9·38 | ·688 | ·485 | ·203 | ·219 |

The figures given in the 5th columns in the Tables, entitled " σ_d ," are simply the differences between the values given in the 3rd and 4th columns. The values of σ_d must be smaller than the true value, since the absorption of the scattered radiations in the materials and also the small amount of scattering in the backward direction were neglected in obtaining σ_d . As previously mentioned, it is impossible, at the present stage, to find the true value of the scattering from the theoretical formula (6) or (6'), unless the law of distribution of the scattered radiation is known. To give an approximate correction, however, to the apparent value S (Tables I. to III.), let us first assume that the absorption correction for obliquity is omitted. Then we have

$$\begin{aligned} S &= \int_0^t I_0 e^{-(\mu+\sigma)x} \sigma e^{-(\mu+\sigma)(t-x)} dx \\ &= I_0 \sigma e^{-(\mu+\sigma)t}. \end{aligned}$$

Hence we have

$$\sigma = \frac{S}{I_0 t e^{-(\mu+\sigma)t}} \quad . \quad . \quad . \quad . \quad . \quad (9)$$

The figures given in the last columns in Tables IV. to VI., entitled " σ_κ ," are the values calculated by formula (9). It is noticeable that these values of σ_κ are generally greater than those obtained as the difference between the values of $\mu + \sigma$ and μ , although the divergence is not very marked. The values of σ_κ and also σ_d increase as the thickness of the radiating plate decreases. This is what we should expect, since the absorption due to obliquity has been neglected. The values of σ in the 5th and 6th columns in Tables IV. to VI. are plotted in fig. 4, and the curves connecting the values of σ_κ for each element continued to cut the axis of σ . There seems to be little doubt that this extrapolation for very thin radiating plates is justified. The values of σ corresponding to very thin plates were taken as the true scattering coefficients. The results are as follows:—

TABLE VII.

| | σ . | $\frac{\sigma}{\rho}$. | $\frac{\sigma}{\rho} / \left(\frac{\sigma}{\rho} \right)_{\text{Al}}$. | $\frac{N^*}{A} / \left(\frac{N}{A} \right)_{\text{Al}}$. | μ . | $\frac{\mu}{\rho}$. |
|---------------|-------------------|-------------------------|--|--|-------------------|-----------------------|
| | cm. ⁻¹ | cm. ² /gr. | | | cm. ⁻¹ | cm. ² /gr. |
| Aluminium ... | ·105 | ·0396 | 1·0 | 1·0 | ·0697 | ·0263 |
| Iron | ·290 | ·0370 | ·93 | ·96 | ·206 | ·0262 |
| Lead | ·345 | ·0304 | ·77 | ·82 | ·460 | ·0423 |

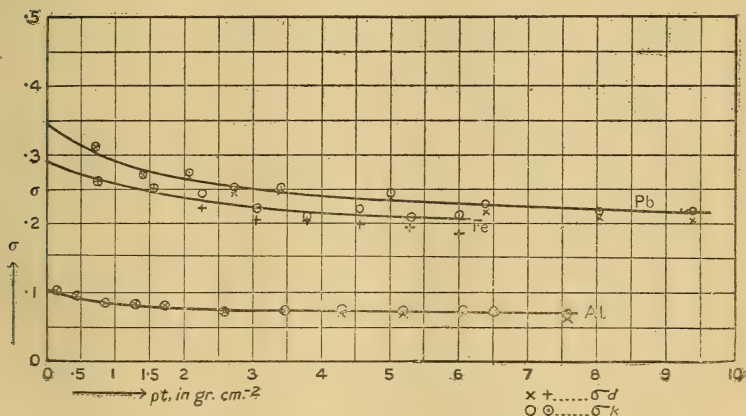
* N = Moseley's atomic number of the element.

A = atomic weight of the element.

The mean value of μ for each element is also given in the Table. The mass scattering σ/ρ and the mass absorption μ/ρ were calculated.

In the calculations given in this paper it has been implicitly assumed that the scattered radiations are exactly of the same type as the primary radiation, and have not suffered any transformation. It should, however, be emphasized that Florance found distinct evidence that there was a real change of type in the radiation which accompanied scattering. For example, he found the radiation scattered backward from the plate was more easily absorbed than primary radiation, and therefore was of longer wave-length. It is difficult to take any account of this transformation in deducing the scattering coefficient. If, however, we disregard the change of type, the radiation scattered backward should be taken into account. It has

Fig. 4.



already been mentioned that the amount of the radiation scattered backwards was about 15 per cent. of the radiation scattered in the forward direction. Making this correction for the observed values, we conclude that the values of σ and σ/ρ are as follows :—

TABLE VIII.

| | σ . | σ/ρ . |
|-----------------|------------|-----------------|
| Aluminium | ·121 | ·045 * |
| Iron | ·334 | ·042 |
| Lead | ·397 | ·034 |

* Florance (Phil. Mag. xxvii. p. 225, 1914) estimated the value of σ/ρ for aluminium to be 0·05 approximately.

§ 5. Conclusions.

(1) We can clearly see from Table VII. that the mass scattering for each element is of roughly the same order of magnitude. This is in a fairly good agreement with the experiments of Florance. The values of σ/ρ , however, were in addition compared with the ratios of Moseley's* "atomic number" of the element divided by the atomic weight of the element. The ratios of $\frac{\sigma}{\rho} / \left(\frac{\sigma}{\rho}\right)_{Al}$ and $\frac{N}{A} / \left(\frac{N}{A}\right)_{Al}$ are given in the 4th and 5th columns in Table VII. respectively. It is very interesting to see that the two ratios for each element are very nearly equal. Moseley's atomic number of the element probably represents the number of electrons exterior to the central nucleus, according to the atomic structure suggested by Sir E. Rutherford†. Taking this to be the case, we can conclude that the scattering of the gamma rays per atom is approximately proportional to the number of the electrons exterior to the nucleus in the atom. Sir J. J. Thomson‡ showed, on theoretical grounds, that the scattering of X rays should be proportional to the number of electrons which were influenced by the primary rays. According to the atomic structure suggested by Sir E. Rutherford, it would be expected that the scattering electrons should be those exterior to the nucleus, and therefore should be equal in number to the atomic number of the element. From Barkla's measurements of scattering of X rays of ordinary frequencies, it is clearly seen that the scattering coefficient is approximately proportional to the atomic number for the elements of atomic weight not greater than 32, including hydrogen. For the elements heavier than sulphur, Barkla's results led to a different conclusion. J. J. Thomson's simple theory of scattering assumes that the scattering electrons are independent of each other when they are influenced by primary rays. This condition would be satisfied only in the case where the displacement of the electrons influenced by the primary rays is very small compared with their mutual distance apart, so that the mutual action is negligible. The deviation from the simple theory of scattering in the heavier elements,

* Moseley, *Phil. Mag.* xxvi. p. 1026 (1913); xxvii. p. 703 (1914).

† Sir E. Rutherford, *Phil. Mag.* xxi. p. 669 (1911).

‡ Sir J. J. Thomson's theory of scattering was given in the first edition of 'Conduction of Electricity through Gases.'

therefore, can be explained if we assume that the electrons are packed very close in the atoms of the elements*. The displacement of the electrons influenced by the primary ray should be also dependent on the wave-length of the rays. When the wave-length is exceedingly short, the duration of the influence on the electrons should be very small, and therefore we might expect that the displacement of the electrons should be exceedingly small. The result of the present paper shows that even heavier elements scatter the gamma rays of exceedingly short wave-length, like light elements scatter the X rays of comparatively long wave-length. This may be considered as a strong support of the above explanation.

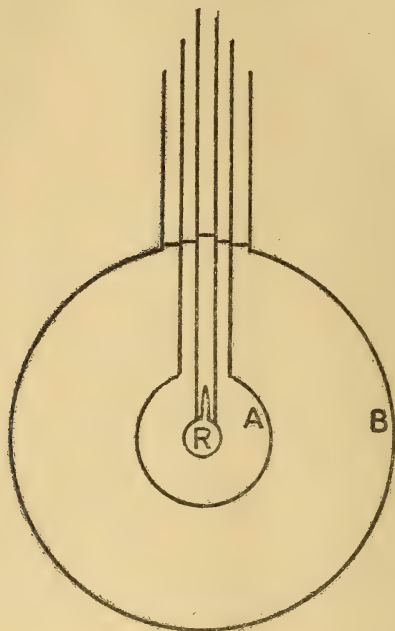
(2) Table VII. shows that the values of μ/ρ and σ/ρ are, for the elements examined, all about the same order of magnitude for the very penetrating gamma rays from radium. Assuming the relation between absorption and wave-length found by Hull and Rice, the true absorption coefficient of gamma rays in aluminium should be small compared with the scattering coefficient; but this does not appear to be the case. Since it is very difficult to determine the values of the corrections to be applied to the observed value of σ/ρ , on account of uncertainty as to the distribution and absorption of the scattered gamma rays, it might be thought possible that, after all, the value of σ/ρ is large compared with μ/ρ , or, in other words, that scattering is predominant in ordinary methods of measuring absorption coefficients of gamma rays. To show that this is not the case, the following simple experiments have been made.

Mercury was contained between two concentric glass spheres A and B (fig. 5), of diameters 6.2 cm. and 2.1 cm. respectively. A small sphere R, of the diameter .77 cm., contained about 80 millicuries of radium emanation, and was kept at the centre of the sphere A, which was filled with mercury. Hence the gamma rays from the source had to penetrate about .67 cm. of mercury, which was nearly equivalent in absorption to the lead plate, 1 cm. thick, in the main experiments described in § 2; so that only the penetrating gamma rays from radium C were used. In this arrangement everything is symmetrical with regard to the source, and therefore not only the primary rays but also the scattered rays should be equally intense in

* Barkla, *Phil. Mag.* xxxi. p. 222 (1916).

all directions. If absorption were negligible in comparison with scattering, the effect in an external electroscope should not be sensibly reduced by the interposition of an additional thickness of mercury; for it is obvious that scattering

Fig. 5.



without absorption should not lead to any diminution of intensity of the rays. The electroscope was the same as that used in the main experiments. The measurements were carried out with and without mercury between A and B. The ionization currents were as follows :—

With mercury : 12·97 div./min.

Without mercury : 48·25 „

The great decrease of the ionization current should be mainly due to the absorption in the mercury. From the observed values, the absorption coefficient was found to be $\mu = 0.64 \text{ cm.}^{-1}$. The value should be a little greater than the true value, since the total amounts of the scattered rays are themselves reduced by absorption.

Another experiment, similar to that described in § 3, was performed with mercury. The mercury was filled in a glass trough, the thickness of the mercury plate being 2.06 cm. The source was the same as that used in the first experiment, but it was screened by a lead plate 1 cm. thick. The ionization current in the electroscope was as follows :—

| | |
|---|----------------|
| The source alone | 100 per cent., |
| The mercury plate in position R ₁ (fig. 2) | 17.71 ,, |
| The mercury plate in position R ₂ (fig. 2) | 31.24 ,, |

which gave :

$$\begin{aligned} \mu + \sigma &= .86 \text{ cm.}^{-1}, & \mu &= .56 \text{ cm.}^{-1}, & S &= 13.5 \text{ p. c.}; \\ \sigma_d &= .30 \text{ cm.}^{-1}, & \sigma_\kappa &= .37 \text{ cm.}^{-1}; \\ \mu\rho &= .041 \text{ cm.}^2 \text{ gr.}^{-1}, & \frac{\sigma_\kappa}{\rho} &= .027 \text{ cm.}^2 \text{ gr.}^{-1}. \end{aligned}$$

The results confirm the above-mentioned conclusion.

In the second experiment only one thickness of mercury was tried, and therefore the final values of σ and μ for small thickness could not be obtained.

(3) Comparison of the scattering coefficients for the ordinary X rays and for the gamma rays of very high frequencies :—In the case of light elements, whose atomic weight is not greater than 32, the absolute values of the mass-scattering of X rays were found to be between 0.1 and 0.4 cm.² gr.⁻¹, and to be about 1.2 cm.² gr.⁻¹ for aluminium by Crowther. For the heavier elements the values were greater, according to Barkla's and Crowther's results. The writer's results in Table VIII. show that the mass-scattering for the gamma rays of very high frequencies is far less than that for the ordinary X-rays. The difference is of great interest, but further investigation is required before any explanation can be offered.

4. The scattering coefficient of the gamma rays of very high frequencies is comparable in value with the true absorption coefficient of an element. This difference between gamma rays and ordinary X rays indicates the importance of taking into account the scattering of gamma rays in all measurements of their absorption by matter.

I wish to express my best thanks to Sir Ernest Rutherford for his kind permission to carry out this research in his laboratory, and for giving me many suggestions during the course of the investigation. My thanks are also due to Mr. Tunstall and Mr. Kay for their kind assistance.

The Physical Laboratory,
Victoria University of Manchester,
November 1916.

IX. *The Energy in the Electromagnetic Field.*

By E. A. BIEDERMANN, B.Sc., A.M.I.E.E.*

THE object of the present paper is to point out certain consequences of the assumption that the magnetic or kinetic energy density in an electromagnetic field is represented by $\mathbf{H}^2/8\pi$, and to suggest a possible modification of this expression. The calculation on the above basis, of the kinetic energy in the field due to any system of spherical charges, either surface or volume, may be effected by elementary methods, as has been shown recently by Prof. Anderson † for the case of point charges, and earlier by Prof. Nicholson ‡ for two or more point charges in the same straight line. Whilst the derivation of the expression for the energy for the somewhat more general case of spherical charges of finite size is not the object of this paper, yet the calculation will be shortly outlined for the sake of completeness, and because certain integrals occurring will be required later.

The energy of a system of charges follows at once from that of a pair by means of the relation

$$\mathbf{H}^2 = \Sigma(\alpha_r^2 + \beta_r^2 + \gamma_r^2) + 2\Sigma\Sigma(\alpha_r\alpha_s + \beta_r\beta_s + \gamma_r\gamma_s), \quad (1)$$

$(\alpha_r, \beta_r, \gamma_r)$, $(\alpha_s, \beta_s, \gamma_s)$, &c., denoting the components of magnetic force at a point due to charges e_r , e_s , &c., respectively. The individual energy of any one of the charges e_r of the system (*i. e.*, the energy associated with that charge when the rest of the system is removed) is, for a spherical

* Communicated by the Author.

† Prof. A. Anderson. Phil. Mag. Aug. 1916.

‡ Prof. Nicholson, Proceedings of the Physical Society, April 1915.

surface charge

$$T_i = \frac{1}{8\pi} \int (\alpha_r^2 + \beta_r^2 + \gamma_r^2) dv = \frac{1}{3} \frac{e_r^2}{a_r} V_r^2, \quad (2)$$

where e_r is expressed in E.M.U.

To calculate the mutual energy of any two charges e_1, e_2 , of radii a_1, a_2 , the distance between them being r , refer them to axes with origin at e_1 , the z -axis coinciding with the line joining the charges. Let $(u_1, v_1, w_1), (u_2, v_2, w_2)$ be the component velocities of the charges, r_1, r_2 their respective distances from any point (x, y, z) , and $(\alpha_1, \beta_1, \gamma_1), (\alpha_2, \beta_2, \gamma_2)$ the components of magnetic force at that point due to the charges respectively. We then have

$$\left. \begin{aligned} \alpha_1 &= \frac{e_1}{r_1^3} (zv_1 - yw_1), & \alpha_2 &= \{(z-r)v_2 - yw_2\} \\ \beta_1 &= \frac{e_1}{r_1^3} (xw_1 - zu_1), & \beta_2 &= \{xw_2 - (z-r)u_2\} \\ \gamma_1 &= \frac{e_1}{r_1^3} (yu_1 - xv_1), & \gamma_2 &= \{yu_2 - xv_2\} \end{aligned} \right\} \quad (3)$$

Denoting by T_m the mutual energy of the charges, we obtain

$$\begin{aligned} T_m &= \frac{1}{4\pi} \int (\alpha_1\alpha_2 + \beta_1\beta_2 + \gamma_1\gamma_2) dv \\ &= \frac{e_1e_2}{4\pi} \iiint \left[(v_1v_2 + w_1w_2)x^2 + (u_1u_2 + w_1w_2)y^2 \right. \\ &\quad \left. + (u_1u_2 + v_1v_2)z(z-r) - (u_1v_2 + v_1u_2)xy \right. \\ &\quad \left. - (v_1w_2 + w_1v_2)yz - (w_1u_2 + u_1w_2)xz \right. \\ &\quad \left. + w_1u_2rx + w_1v_2ry \right] \frac{dx dy dz}{r_1^3 r_2^3}, \end{aligned}$$

the integration extending throughout all space external to the charges. Since the axis of z coincides with the line joining the charges, most of the integrals evidently vanish by symmetry and the expression reduces to

$$T_m = \frac{e_1e_2}{4\pi} \{ (u_1u_2 + v_1v_2 + 2w_1w_2)I_1 + (u_1u_2 + v_1v_2)I_2 \}, \quad (4)$$

where

$$I_1 = \iiint \frac{x^2}{r_1^3 r_2^3} dx dy dz = \iiint \frac{y^2}{r_1^3 r_2^3} dx dy dz,$$

and

$$I_2 = \iiint \frac{z(z-r)}{r_1^3 r_2^3} dx dy dz.$$

These integrals are easily evaluated by transforming to polar co-ordinates with origin at e_1 , and integrating first with respect to ϕ , then with respect to r_2 treated as an independent variable by means of the relation

$$r_2^2 = r_1^2 + r^2 - 2r_1 r \cos \theta$$

(r_2 being of course regarded as positive for all points), and finally with respect to r_1 . The results are

$$\left. \begin{aligned} I_1 &= \iiint \frac{x^2}{r_1^3 r_2^3} dx dy dz = \frac{2\pi}{3r} \left\{ 3 - \left(\frac{a_1^2 + a_2^2}{r^2} \right) \right\} \\ I_2 &= \left(\iiint \frac{z(z-r)}{r_1^3 r_2^3} dx dy dz = \frac{4\pi}{3r} \left(\frac{a_1^2 + a_2^2}{r^2} \right) \right) \end{aligned} \right\}. \quad (5)$$

From (1), (2), (4), and (5) we obtain for the total kinetic energy of the system

$$\begin{aligned} T &= \frac{1}{3} \sum \frac{e_r^2}{a_r} (u_r^2 + v_r^2 + w_r^2) \\ &+ \frac{1}{2} \sum \sum \frac{e_r e_s}{r_{rs}} \left\{ (u_r u_s + v_r v_s + 2w_r w_s) \right. \\ &\quad \left. + \frac{1}{3} (u_r u_s + v_r v_s - 2w_r w_s) \left(\frac{a_r^2 + a_s^2}{r^2} \right) \right\}, \quad (6) \end{aligned}$$

the double summation sign denoting that the charges are to be taken in every possible way in *pairs*. If the charges are spherical uniform *volume* charges instead of *surface* charges, it is easily shown that the coefficient of $\frac{e_r^2}{a_r}$ becomes $\frac{2}{3}$,

and that of $\left(\frac{a_r^2 + a_s^2}{r^2} \right)$ becomes $\frac{1}{5}$ instead of $\frac{1}{3}$.

Now let these results be applied to the case of two circuits carrying currents.

Neglecting terms containing the factor $\left(\frac{a_r^2 + a_s^2}{r^2}\right)$, as we may do owing to the extreme smallness of the charges concerned, the mutual energy of the two circuits is seen to be

$$T_m = \frac{1}{2} \sum \sum \frac{e_1 e_2}{r} (u_1 u_2 + v_1 v_2 + 2w_1 w_2), \quad . \quad . \quad (6A)$$

the suffix 1 referring to charges in one circuit, the suffix 2 to those in the other.

The above expression is equivalent to

$$T_m = \frac{1}{2} i_1 i_2 \iint \frac{\cos \epsilon}{r} ds_1 ds_2 + \frac{1}{2} i_1 i_2 \iint \frac{\cos \alpha_1 \cos \alpha_2}{r} ds_1 ds_2, \quad . \quad (7)$$

where ϵ is the angle between the elements ds_1, ds_2 of the two circuits, and α_1, α_2 are the angles these elements make with the line joining them.

But it is well known as the result of experiment, or as an immediate deduction from experiment, that the mutual energy of two circuits is given by

$$T_m = i_1 i_2 \iint \frac{\cos \epsilon}{r} ds_1 ds_2, \quad . \quad . \quad . \quad (8)$$

Expressions (7) and (8) are, however, not in general equivalent. This discrepancy leads one to question whether $\mathbf{H}^2/8\pi$ is a true representation of the kinetic energy density. This value is apparently an immediate deduction from the two fundamental circuital laws of electromagnetism. From the law of electromagnetic induction we deduce that the energy in the field due to a system of circuits is $\frac{1}{2} \sum i \phi$, where ϕ is the magnetic flux linked with the circuit carrying the current i . The circuital law connecting magnetic force and current then shows that this expression is equal to $\int \frac{\mathbf{H}^2}{8\pi} dv$ taken throughout all space. But what does

\mathbf{H} here really represent? It represents *not* the actual magnetic force at a point at a *given instant*, but the *mean* value of this force at the point, for it is now known that the charge whose motion constitutes a current is not distributed uniformly throughout the conducting substance, but is concentrated in a number of discrete particles, so that the magnetic force at a point is not constant. In

any ordinary circuit the number of moving electric particles is such a large one that the variation of magnetic force is negligible at all points external to the conductor, but within the conductor this is no longer the case. At such points the square of the mean value of the magnetic force is not equal to the mean value of the square of the instantaneous magnetic force.

Expression (8) is the result of calculation on the former basis, whilst (7) has been deduced on the latter basis. Hence the two results are not identical. This, the author suggests, is the explanation of the discrepancy.

Experiment proves, however, that (8), which is in effect the result of integrating over all space the square of the mean value of the magnetic force at a point, correctly expresses the mutual energy of two circuits. But (7) is the result of integrating the square of the instantaneous magnetic force and then taking the mean with regard to time, this being in reality what is done when (7) is substituted for (6 A). It follows that $\mathbf{H}^2/8\pi$ does not represent the kinetic energy density in the field, if by \mathbf{H} is understood the *instantaneous* value of the magnetic force.

What, then, may be taken to be the true representation of the kinetic energy density at any given point?

Let \mathbf{G} denote $\frac{1}{c} \sum \mathbf{R} \mathbf{V} \cos \theta$ where \mathbf{R} is the electric intensity in E.S.U. at a point due to any single charge, and θ the angle between the directions of \mathbf{R} and the velocity \mathbf{V} of the charge. Then

$$\mathbf{G}^2 = \left(\frac{1}{c} \sum \mathbf{R} \mathbf{V} \cos \theta \right)^2 = \sum g_r^2 + 2 \sum \sum g_r g_s,$$

where

$$g_r = \frac{1}{c} \mathbf{R}_r \mathbf{V}_r \cos \theta_r, \quad g_s =, \text{ \&c.}$$

Referring the system as before to axes with origin at e_1 , and having the line joining e_1, e_2 for z -axis, we have

$$g_1 = \frac{e_1}{r_1^3} (u_1 x + v_1 y + w_1 z),$$

$$g_2 = \frac{e_2}{r_2^3} \{u_2 x + v_2 y + w_2 (z - r)\}.$$

For spherical surface charges of radii a_1, a_2 , &c., we get

$$\int \frac{g_1^2}{8\pi} dv = \frac{1}{6} \frac{e_1^2}{a_1} (u_1^2 + v_1^2 + w_1^2), \quad \dots \quad (9)$$

the integration being over all space external to the charges.

Again,

$$\begin{aligned} \int \frac{g_1 g_2}{4\pi} dv = & \frac{e_1 e_2}{4\pi} \left[u_1 u_2 \iiint \frac{x^2}{r_1^3 r_2^3} dx dy dz \right. \\ & \left. + v_1 v_2 \iiint \frac{y^2}{r_1^3 r_2^3} dx dy dz + w_1 w_2 \iiint \frac{z(z-r)}{r_1^3 r_2^3} dx dy dz \right], \end{aligned}$$

all the other integrals vanishing by symmetry,

$$\therefore \int \frac{g_1 g_2}{4\pi} dv = \frac{e_1 e_2}{4\pi} \{ (u_1 u_2 + v_1 v_2) I_1 + w_1 w_2 I_2 \}, \quad (10)$$

where I_1, I_2 denote the same integrals as before.

From (4), (10), and (5) we find

$$\begin{aligned} \frac{1}{4\pi} \int (\alpha_1 \alpha_2 + \beta_1 \beta_2 + \gamma_1 \gamma_2 + g_1 g_2) dv \\ = \frac{e_1 e_2}{4\pi} (u_1 u_2 + v_1 v_2 + w_1 w_2) (2I_1 + I_2) \\ = \frac{e_1 e_2 (u_1 u_2 + v_1 v_2 + w_1 w_2)}{r}. \end{aligned}$$

Adding (2) and (9) for e_1 and e_2 , and summing for all charges, we obtain finally

$$\begin{aligned} \int \frac{(\mathbf{H}^2 + \mathbf{G}^2)}{8\pi} dv = & \frac{1}{2} \sum \frac{e_r^2}{a_r} (u_r^2 + v_r^2 + w_r^2) \\ & + \sum \sum \frac{e_r e_s}{r} (u_r u_s + v_r v_s + w_r w_s). \quad \dots \quad (11) \end{aligned}$$

The mutual value of $\int \frac{(\mathbf{H}^2 + \mathbf{G}^2)}{8\pi} dv$ for two circuits is

$$\sum \sum \frac{e_1 e_2}{r} (u_1 u_2 + v_1 v_2 + w_1 w_2) = i_1 i_2 \iint \frac{\cos \epsilon}{r} ds_1 ds_2,$$

which is identical with (8). Thus, by assuming that the instantaneous kinetic energy density at any point is represented by $\frac{1}{8\pi} (\mathbf{H}^2 + \mathbf{G}^2)$, we should find a correct value for

the mutual energy of two circuits. It is suggested, therefore, that this may be a correct representation of the instantaneous kinetic energy density in all cases. The argument, in fact, is identical with that used when we conclude from the theory of point charges of magnetism that the energy density is $\mathbf{H}^2/8\pi$. In the theory of magnetism, however, \mathbf{H} is regarded as constant at a given point (for a static system of magnets) whether without or within magnetic matter, because the latter is treated as capable of infinite subdivision into elements of magnetic moment Idv .

This is analogous to assuming the moving electricity in a circuit to be continuously distributed throughout the substance of the conductor. In such a case, at any given point,

$$\begin{aligned} \mathbf{G} &= \frac{1}{c} \sum \mathbf{R} \mathbf{V} \cos \theta = \iiint \rho \mathbf{V} \frac{d}{ds} \left(\frac{1}{r} \right) dx dy dz \\ &= \int \rho \mathbf{V} da \int \frac{d}{ds} \left(\frac{1}{r} \right) ds = 0, \end{aligned}$$

the circuit being supposed divided into an infinite number of filaments carrying currents $\rho \mathbf{V} da$, and the integration extended throughout the conductor. Thus for a uniform distribution of the moving charge throughout each filament of the conductor \mathbf{G} vanishes at all points both without and within the conductor, and \mathbf{H} at any point is constant. Actually the charge is not so distributed, and \mathbf{G} has a finite and appreciable value within the conductor.

The value arrived at for the kinetic energy of a system on the above assumption for the energy density leads to some interesting results.

For a system of spherical surface charges, having a common velocity \mathbf{V} both in magnitude and direction,

$$\mathbf{T} = \left\{ \sum \frac{1}{2} \frac{e_r^2}{a_r} + \sum \sum \frac{e_r e_s}{r} \right\} \mathbf{V}^2 = \mathbf{W} \frac{\mathbf{V}^2}{c^2},$$

where \mathbf{W} is the electrostatic potential energy of the system, if supposed at rest in its instantaneous position. This result is perfectly general whether we suppose the charges

spherical or not. For

$$\begin{aligned} \mathbf{H}^2 + \mathbf{G}^2 &= \frac{1}{c^2} (\Sigma[\mathbf{RV}])^2 + \frac{1}{c^2} (\Sigma(\mathbf{RV}))^2 \\ &= \frac{1}{c^2} \{[\mathbf{RV}]^2 + (\mathbf{RV})^2\} = \frac{V^2}{c^2} R^2, \end{aligned}$$

where R now denotes the *resultant* electric intensity.

$$\therefore \int \frac{(\mathbf{H}^2 + \mathbf{G}^2)}{8\pi} dv = \frac{V^2}{c^2} \int \frac{R^2}{8} dv = W \frac{V^2}{c^2}. \quad (12)$$

From this it appears that the mass of the system is the same as if each Faraday tube had a mass $R^2/4\pi c^2$ per unit volume, whilst on the basis that the kinetic energy in the field is only $\int \frac{\mathbf{H}^2}{8\pi} dv$, the conclusion arrived at is that the apparent density of these tubes varies from the above value for motion at right angles to the tubes down to zero for motion in the direction of the tubes. The result arrived at above suggests the possibility of the propagation of disturbances other than transverse ones.

Expression (11) for the energy in the field is easily extended to cover any distribution of electricity whatever the velocities of its elements. Imagine it divided into infinitesimal spheres of various sizes. It is easily shown that for a system of spherical *volume* charges

$$\begin{aligned} T &= \int \frac{(\mathbf{H}^2 + \mathbf{G}^2)}{8\pi} dv = \frac{3}{5} \Sigma \frac{e_r^2}{a_r} (u_r^2 + v_r^2 + w_r^2) \\ &\quad + \Sigma \Sigma \frac{e_r e_s}{r} (u_r u_s + v_r v_s + w_r w_s). \end{aligned}$$

If ρ_1 denote the density of the charge (in E.M.U.) in one of the spheres of volume dv_1 , and therefore of radius

$$\left(\frac{3}{4\pi} dv_1 \right)^{1/3},$$

$$\begin{aligned} T &= \frac{3}{5} \left(\frac{4\pi}{3} \right)^{1/3} \int \rho_1^2 (u_1^2 + v_1^2 + w_1^2) (dv_1)^{5/3} \\ &\quad + \frac{1}{2} \iint \frac{\rho_1 \rho_2 (u_1 u_2 + v_1 v_2 + w_1 w_2)}{r} dv_1 dv_2, \end{aligned}$$

the coefficient $\frac{1}{2}$ now entering because $\Sigma \Sigma$ indicated that

the charges were to be taken in every possible way in pairs.

The first integral vanishes in the limit, so that

$$T = \frac{1}{2} \iint \frac{\rho_1 \rho_2 (u_1 u_2 + v_1 v_2 + w_1 w_2)}{r} dv_1 dv_2. \quad (13)$$

If we assume that the principles of least action and the conservation of energy hold for the electromagnetic field, we could apply Lagrange's equations directly to the above expression for the kinetic energy combined with that for the electrostatic potential energy. We could not expect, however, to obtain by this means results of complete generality, since the above expression was deduced from others for \mathbf{H} and \mathbf{G} , which took no account of the fact that electromagnetic disturbances are propagated with finite velocity. To obtain the general equations of the electromagnetic field, this fact must be allowed for.

Let the system be supposed to include at the point (x, y, z) at time t a small spherical surface charge of radius a moving with velocity (U, V, W) .

Expression (13) may then be written in the form

$$T = \frac{1}{2} \frac{e^2}{ac^2} (U^2 + V^2 + W^2) + \frac{e}{c^2} \int \frac{\rho}{r} (Uu + Vv + Ww) dv + T_0,$$

whilst the electrostatic potential energy is given by

$$W = e \int \frac{\rho}{r} dv + W_0,$$

e being now expressed in E.S.U., and T_0, W_0 denoting those parts of the kinetic and potential energies which are independent of the co-ordinates of e .

Allowing now for the finite velocity of propagation by substituting $[\rho u]$ for ρu , &c., and $[\rho]$ for ρ , the square brackets having the usual meaning, we get

$$\begin{aligned} L = T - W &= \frac{1}{2} \frac{e^2}{ac^2} (U^2 + V^2 + W^2) \\ &+ \frac{e}{c^2} \int \frac{\{U[\rho u] + V[\rho v] + W[\rho w]\}}{r} dv \\ &- e \int \frac{[\rho]}{r} dv + L_0. \end{aligned}$$

The Lagrangian operator then gives

$$\begin{aligned} \frac{e^2}{ac^2} \frac{dU}{dt} + \frac{e}{c^2} \frac{d}{dt} \int \frac{[\rho u]}{r} dv \\ - \frac{e}{c^2} \frac{\partial}{\partial x} \int \frac{\{U[\rho u] + V[\rho v] + W[\rho w]\}}{r} dv \\ + e \frac{\partial}{\partial x} \int \frac{[\rho]}{r} dv = 0 \end{aligned}$$

with corresponding equations for the y , z co-ordinates.. Since $\frac{e^2}{ac^2}$ is the mass of the charge e , these equations give for the force on unit E.S. charge at *rest*

$$X = - \frac{1}{c} \frac{d}{dt} \frac{1}{c} \int \frac{[\rho u]}{r} dv - \frac{\partial}{\partial x} \int \frac{[\rho]}{r} dv, \quad Y, \text{ \&c.},$$

and for the *additional* force on the charge e due to its *motion*

$$\begin{aligned} P = - \frac{e}{c} \left(U \frac{\partial}{\partial x} + V \frac{\partial}{\partial y} + W \frac{\partial}{\partial z} \right) \frac{1}{c} \int \frac{[\rho u]}{r} dv \\ + \frac{e}{c} \left\{ U \frac{\partial}{\partial x} \frac{1}{c} \int \frac{[\rho u]}{r} dv + V \frac{\partial}{\partial x} \frac{1}{c} \int \frac{[\rho v]}{r} dv \right. \\ \left. + W \frac{\partial}{\partial x} \frac{1}{c} \int \frac{[\rho w]}{r} dv \right\}, \quad Q, \text{ \&c.}, R, \text{ \&c.} \end{aligned}$$

$$\therefore X = - \frac{1}{c} \frac{dF}{dt} - \frac{\partial \psi}{\partial x}, \quad Y, \text{ \&c.}, \quad \dots \quad (14)$$

and

$$\begin{aligned} P = \frac{e}{c} \left\{ V \left(\frac{\partial}{\partial x} \frac{1}{c} \int \frac{[\rho v]}{r} dv - \frac{\partial}{\partial y} \frac{1}{c} \int \frac{[\rho u]}{r} dv \right) \right. \\ \left. - W \left(\frac{\partial}{\partial z} \frac{1}{c} \int \frac{[\rho u]}{r} dv - \frac{\partial}{\partial x} \frac{1}{c} \int \frac{[\rho w]}{r} dv \right) \right\} \\ = \frac{e}{c} \left\{ V \left(\frac{\partial G}{\partial x} - \frac{\partial F}{\partial y} \right) - W \left(\frac{\partial F}{\partial z} - \frac{\partial H}{\partial x} \right) \right\}, \quad Q, \text{ \&c.}, R, \text{ \&c.}, \quad (15) \end{aligned}$$

where

$$F, G, H = \frac{1}{c} \int \frac{[\rho u]}{r} dv, \text{ \&c.,}$$

and

$$\psi = \int \frac{[\rho]}{r} dv.$$

(14) is the usual expression for the electric intensity in terms of the vector and electric potentials \mathbf{A} , ψ , whilst the three equations (15) give

$$(P, Q, R) = \frac{e}{c} [\mathbf{VH}], \quad . \quad . \quad . \quad (16)$$

where

$$\mathbf{H} = \text{curl } \mathbf{A}, \quad . \quad . \quad . \quad (17)$$

(16) being the well-known value for the force on a charge due to its motion in a magnetic field given in terms of the vector potential by relation (17).

Differentiation of equations (14) combined with the known values of F, G, H , and the relation (17), gives the remaining equations

$$\frac{1}{c} \frac{\partial X}{\partial t} + \frac{4\pi\rho}{c} = \frac{\partial \gamma}{\partial y} - \frac{\partial \beta}{\partial z}, \text{ \&c.}$$

The above is not, of course, an independent derivation of Maxwell's equations, since it has been necessary to introduce the assumption of propagation with finite velocity c . It is, however, significant that, when this assumption is made, Maxwell's equations are derived by applying Lagrange's equations to a Lagrangian function obtained by assuming the kinetic energy in the field to be $\int \frac{(\mathbf{H}^2 + \mathbf{G}^2)}{8\pi} dv$, and the potential energy to be equal to the electrostatic energy of the system.

In the case of slow uniform motion, neglecting the finite velocity of propagation, we had α, β, γ given by

$$\left\{ \frac{\partial}{\partial y} \frac{1}{c} \int \frac{\rho w}{r} dv - \frac{\partial}{\partial z} \frac{1}{c} \int \frac{\rho v}{r} dv \right\}, \text{ \&c.,}$$

and

$$\mathbf{G} \text{ by } \frac{1}{c} \Sigma \mathbf{RV} \cos \theta$$

$$= - \left\{ \frac{\partial}{\partial x} \frac{1}{c} \int \frac{\rho u}{r} dv + \frac{\partial}{\partial y} \frac{1}{c} \int \frac{\rho v}{r} dv + \frac{\partial}{\partial z} \frac{1}{c} \int \frac{\rho w}{r} dv \right\},$$

whilst the most general expressions for α , β , γ are

$$\left\{ \frac{\partial}{\partial y} \frac{1}{c} \int \frac{[\rho w]}{r} dv - \frac{\partial}{\partial z} \frac{1}{c} \int \frac{[\rho v]}{r} dv \right\}, \text{ \&c.}$$

It appears, then, that the generalized expression for \mathbf{G} must be taken to be

$$\begin{aligned} \mathbf{G} = - \left\{ \frac{\partial}{\partial x} \frac{1}{c} \int \frac{[\rho u]}{r} dv + \frac{\partial}{\partial y} \frac{1}{c} \int \frac{[\rho v]}{r} dv + \frac{\partial}{\partial z} \frac{1}{c} \int \frac{[\rho w]}{r} dv \right\} \\ = - \left(\frac{\partial F}{\partial x} + \frac{\partial G}{\partial y} + \frac{\partial H}{\partial z} \right) = \frac{1}{c} \frac{d\psi}{dt}, \end{aligned}$$

so that the kinetic energy density in the field is expressed in its most general form by

$$\frac{1}{8\pi} (\mathbf{H}^2 + \mathbf{G}^2) = \frac{1}{8\pi} \{ (\text{curl } \mathbf{A})^2 + (\text{div } \mathbf{A})^2 \}.$$

X. The Focometry of Lens-Combinations.

By Prof. A. ANDERSON, M.A.*

IT is probably not possible to improve much on the ordinary nodal-slide method of measuring the focal length of a converging or diverging lens-combination. This consists in allowing beams of light from an object, which are made parallel beams by a convex lens, to pass through the combination, which then, either directly or by the help of a convex lens, forms an image of the object on a screen. A vertical line intersecting the axis of the combination, about which a small rotation of the combination produces no displacement of the image, is then found. This vertical line intersects the axis of the combination in H_2 , the second principal point. The image formed on the screen, or, in the case where a convex auxiliary lens is used, the conjugate of this image with respect to the lens, is F_2 , the second principal focus. H_2F_2 is the focal length.

* Communicated by the Author.

and, consequently, H_2H_1 is also divided externally by O in a ratio equal to the magnification. The position of O thus depends on the magnification. If this is zero, O coincides with H_2 (as in the ordinary way of using the nodal slide); if it is infinity, O coincides with H_1 . If O is to the left of H_2 , the magnification lies between unity and zero, and if to the right of H_1 , between $+\infty$ and unity. If it lies between H_2 and H_1 the magnification is negative, and may have any value between zero and $-\infty$.

The position of O can be found with the nodal slide, and then OP_1 and OP_2 can be measured, thus determining the magnification either for a converging or diverging combination. The combination can then be displaced towards or away from the object, the new position of O found, and the corresponding value of the magnification. The focal length and the positions of the cardinal points can then be found by calculation.

The following example of a rough determination of the focal length of a diverging combination will make the method clear. An auxiliary convex lens was used, which enabled an image to be formed on a screen and the position of P_2 to be found. O having been determined with the nodal slide, OP_1 was found to be 51.0 cm. and OP_2 9.0 cm. The combination was then moved towards P_1 and O again determined. OP_2 was then 9.5 cm., OP_1 24.5 cm., and the distance through which the combination was moved 26.9 cm.

$$\text{Thus} \quad \frac{1}{m_1} = 5.7, \quad \frac{1}{m_2} = 2.6,$$

$$\text{and} \quad f = \frac{26.9}{3.1} = 8.7 \text{ cm.}$$

The advantages of the method are that there is no adjustment for parallel light, and no transparent scales necessary for measuring the magnification, which is more accurately determined by measuring OP_1 and OP_2 .

XI. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from vol. xxxii. p. 528.]

November 8th, 1916.—Dr. Alfred Harker, F.R.S., President,
in the Chair.

THE following communication was read:—

'*Aulina rotiformis*, gen. et sp. nov., *Phillipsastrœa hennahi* (Lonsdale), and the Genus *Orionastrœa*.' By Stanley Smith, B.A., D.Sc., F.G.S.

Mr. J. W. JACKSON exhibited a number of facettèd pebbles from Pendleton (Lancashire), and stated that nearly 200 of these had been collected during the last six months from near the top of a section of current-bedded and faulted Glacial Sand and Gravel at an altitude of about 200 feet O.D.

The pebbles occur *in situ* some 2 or 3 feet below the capping of darker subsoil, which contains cores and flakes of flint, including pigmies. They consist of slate, granites (Eskdale and Shap), Ennerdale granophyre, Borrowdale volcanic tuffs, porphyries, quartzites, Millstone Grit, sandstones, Chalk flints, Carboniferous chert, and other rocks.

The largest facettèd pebble measures $11\frac{1}{2} \times 8\frac{1}{4}$ inches, and is 7 inches high; the smallest is only half an inch in diameter.

The facets are generally concave, grooved, or fluted. They vary in number: some stones have one facet only, others two or more. One stone with a flat top shows five incipient facets. On some the grooving is of the nature of parallel series of elongated pits.

Differentiation, according to varying hardness and composition, is well displayed on the granites, porphyries, grits, etc., where the weaker constituents have been strongly eroded, leaving the stones with an irregularly pitted surface.

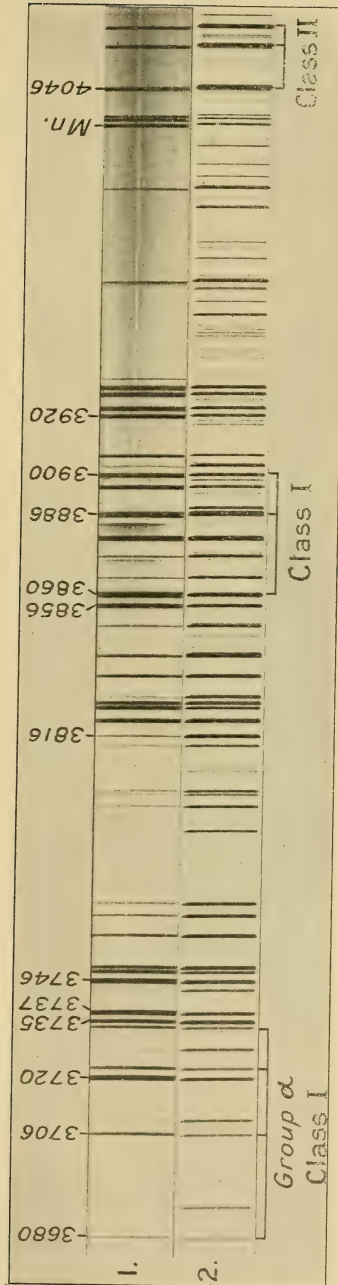
The production of facets by splitting along joint-planes is seen on some examples of sandstone; but the facet thus formed has been modified by wind-action.

A few pebbles occurred in the sand completely inverted, and some show distinct facetting on both sides.

Of examples orientated *in situ*, the facets faced north-westwards, westwards, and south-westwards—the directions of the present prevailing winds.

All the pebbles are of Glacial origin, but the facetting may be relatively quite recent. The upper part of the sands where they occur may be the result of redistribution by wind before a soil-cap began to form.

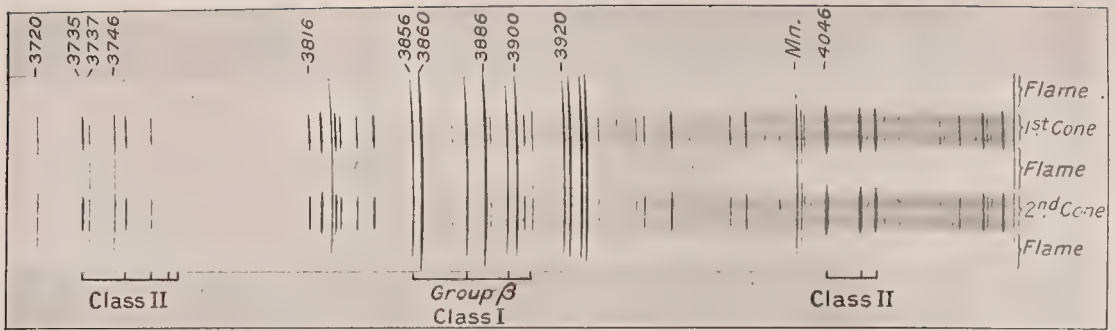
Fig. 3.



Spectra of Iron.

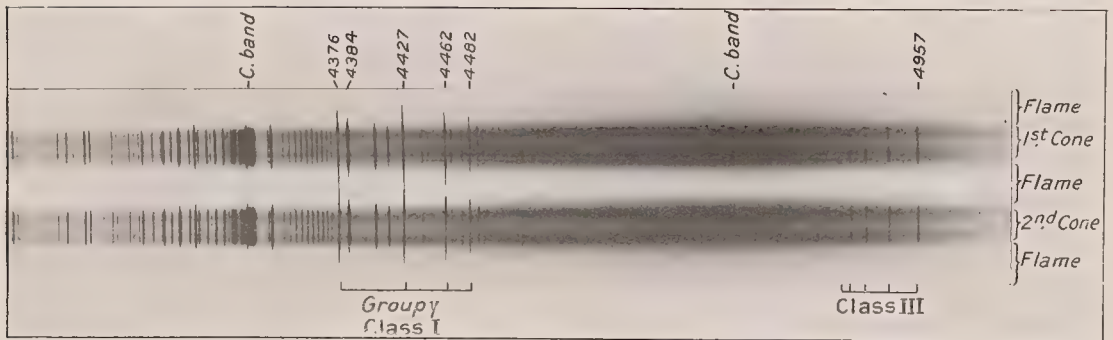
1. Oxy-Acetylene Flame.
2. Self-Induction Spark.

Fig. 1.



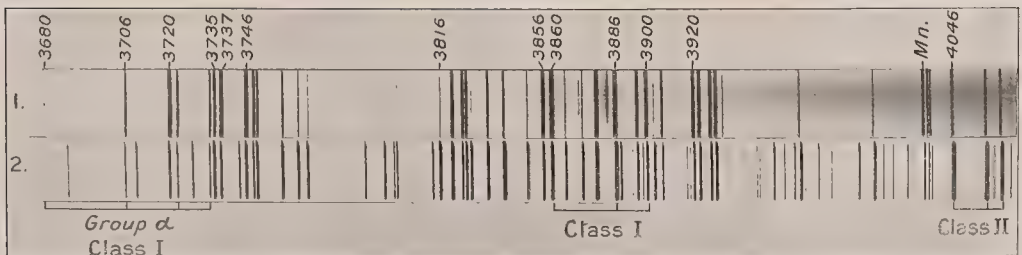
Spectra emitted by Iron Vapour in the air-coal gas flame.

Fig. 2.



Spectra emitted by Iron Vapour in the air-coal gas flame.

Fig. 3.



Spectra of Iron.

1. Oxy-Acetylene Flame.
2. Self-Induction Spark.

BEATT

l. Mag. Ser. 6, Vol. 33, Pl. II.

FIG. 7.



FIG. 5.

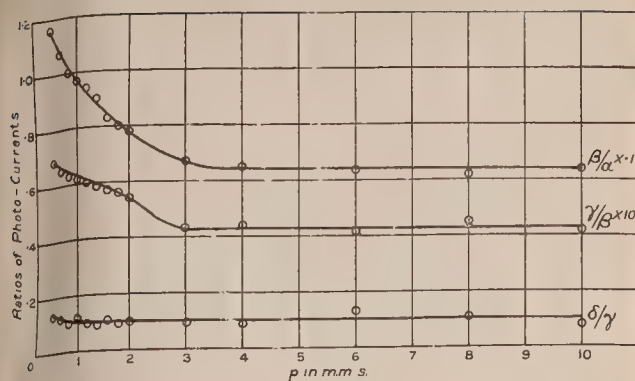


FIG. 6.

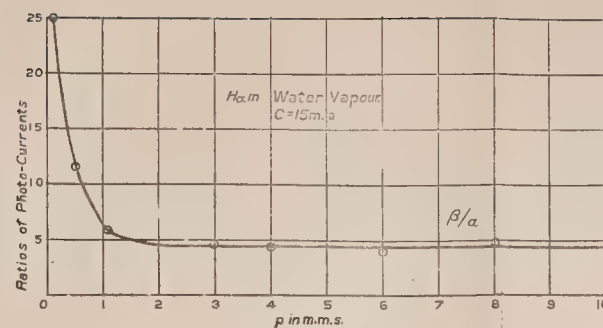


FIG. 7 E.

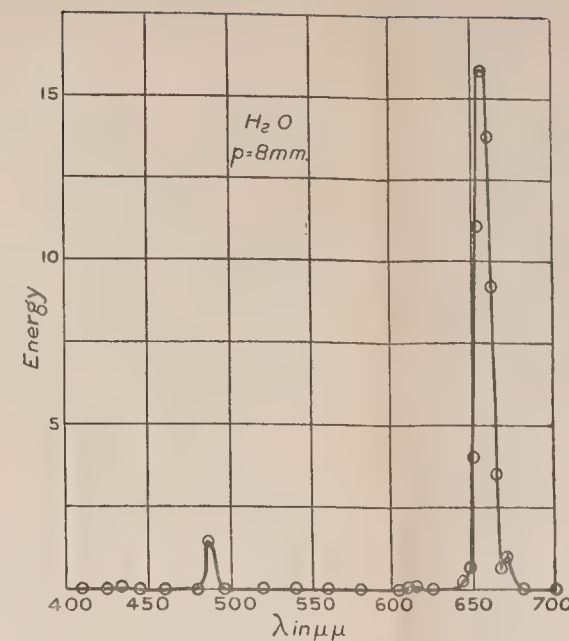


FIG. 7.

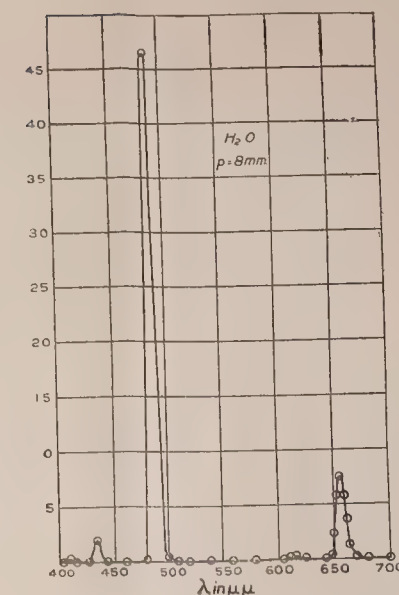


FIG. 8 E.

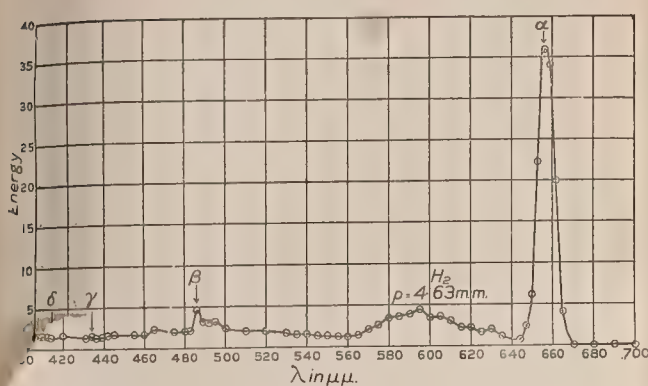


FIG. 8.

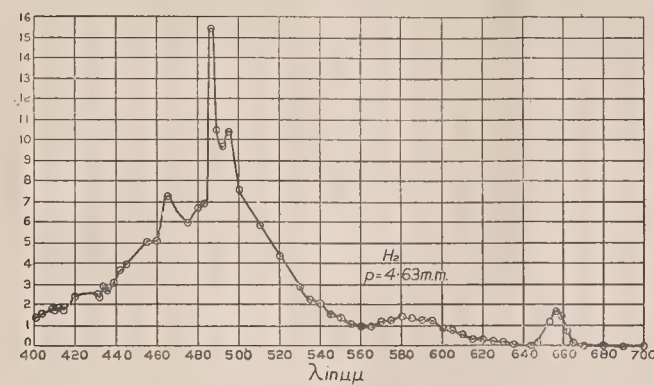


FIG. 11.

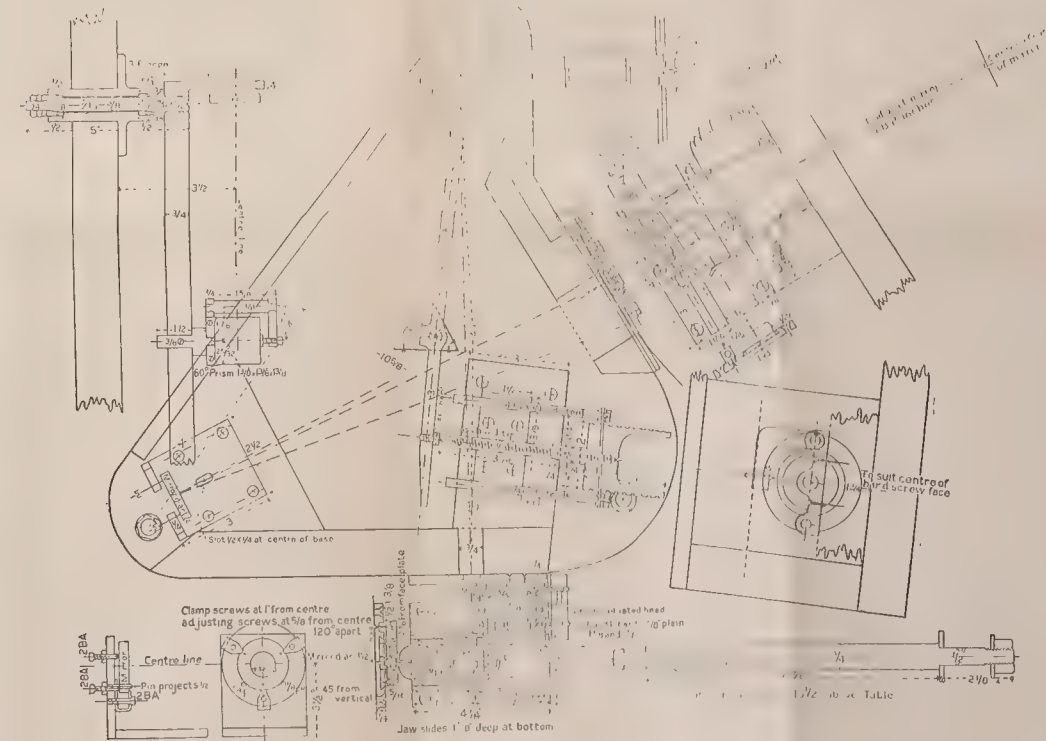


FIG. 9.

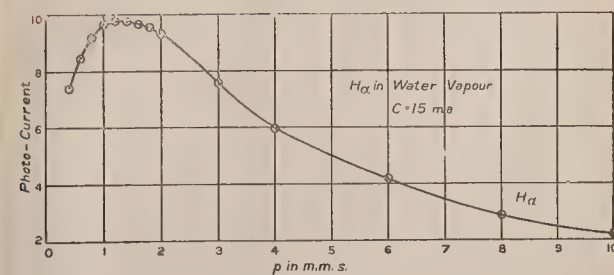
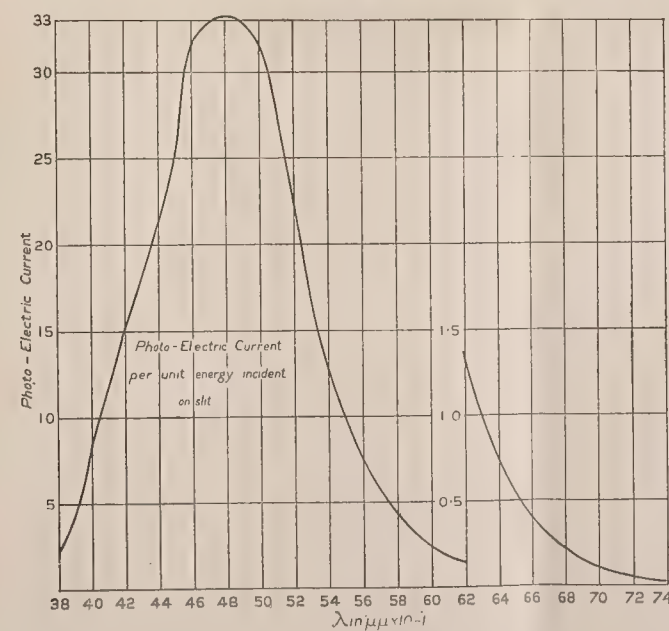


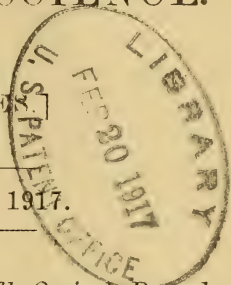
FIG. 10.



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XII. *On Methods for detecting small Optical Retardations, and on the Theory of Foucault's Test.* By Lord RAYLEIGH, O.M., F.R.S.*

AS was, I think, first emphasized by Foucault, the standard of accuracy necessary in optical surfaces is a certain fraction of the wave-length (λ) of the light employed. For glass surfaces refracting at nearly perpendicular incidence the error of linear retardation is about the half of that of the surface; but in the case of perpendicular reflexion the error of retardation is the double of that of the surface. The admissible error of retardation varies according to circumstances. In the case of lenses and mirrors affected with "spherical aberration," an error of $\frac{1}{4}\lambda$ begins to influence the illumination at the geometrical focus, and so to deteriorate the image. For many purposes an error less than this is without importance. The subject is discussed in former papers†.

But for other purposes, especially when measurements are in question, a higher standard must be insisted on. It is well known that the parts of the surfaces actually utilized in interferometers, such as those of Michelson and of Fabry and Perot, should be accurate to $\frac{1}{10}\lambda$ to $\frac{1}{20}\lambda$, and that a still higher degree of accuracy would be advantageous. Even

* Communicated by the Author.

† Phil. Mag. vol. viii. pp. 403, 477 (1879); 'Scientific Papers,' vol. i. p. 414, §§ 3, 4.

under difficult conditions interference-bands may be displayed in which a local departure from ideal straightness amounting to $\frac{1}{20}$ of the band period can be detected on simple inspection. I may instance some recent observations in which the rays passing a fine vertical slit backed by a common paraffin-flame fell upon the object-glass of a 3-inch telescope placed some 20 feet away at the further end of a dark room. No collimator was needed. The object-glass was provided with a cardboard cap, pierced by two vertical slits, each $\frac{1}{10}$ inch wide, and so placed that the distance between the inner edges was $\frac{8}{10}$ inch. The parallelism of the three slits could be tested with a plumb-line. To observe the bands formed at the focus of the object-glass, a high magnifying-power is required. This was afforded by a small cylinder lens, acting as sole eyepiece, whose axis is best adjusted by trial to the required parallelism with the slits. Fairly good results were obtained with a glass tube of external diameter equal to about 3 mm., charged with water or preferably nitro-benzol. Latterly, I have used with advantage a solid cylinder lens of about the same diameter kindly placed at my disposal by Messrs. Hilger. With this arrangement a wire stretched horizontally across the object-glass in front of the slits is seen in fair focus. When the adjustment is good, the bands are wide and the blacknesses well developed, so that a local retardation of $\frac{1}{20}\lambda$ or less is evident if suitably presented. The bands are much disturbed by heated air rising from the hand held below the path of the light.

The necessity for a high magnifying-power is connected with the rather wide separation of the interfering pencils as they fall upon the object-glass. The conditions are most favourable for the observation of very small retardations when the interfering pencils travel along precisely the same path, as may happen in the interference of polarized light, whether the polarization be rectilinear, as in ordinary double refraction, or circular, as along the axis of quartz. In some experiments directed to test whether "motion through the æther causes double refraction"*, it appeared that a relative retardation of the two polarized components could be detected when it amounted to only $\lambda/12000$, and, if I remember rightly, Brace was able to achieve a still higher sensibility. The sensibility would increase with the intensity of the light employed and with the transparency of the optical parts (nicols, &c.), and it can scarcely be said that there is any theoretical limit.

* Phil. Mag. vol. iv. p. 678 (1902); 'Scientific Papers,' vol. v. p. 66.

Another method by which moderately small retardations can be made evident is that introduced by Foucault* for the figuring of optical surfaces. According to geometrical optics rays issuing from a point can be focussed at another point, if the optical appliances are perfect. An eye situated just behind the focus observes an even field of illumination; but if a screen with a sharp edge is gradually advanced in the focal plane, all light is gradually cut off, and the entire field becomes dark simultaneously. At this moment any irregularity in the optical surfaces, by which rays are diverted from their proper course so as to escape the screening, becomes luminous; and Foucault explained how the appearances are to be interpreted and information gained as to the kind of correction necessary. He does not appear to have employed the method to observe irregularities arising otherwise than in optical surfaces, but H. Draper, in his memoir of 1864 on the Construction of a Spherical Glass Telescope†, gives a picture of the disturbances due to the heating action of the hand held near the telescope mirror. Töpler's work dates from the same year, and in subsequent publications‡ he made many interesting applications, such as to sonorous waves in air originating in electric sparks, and further developed the technique. His most important improvements were perhaps the introduction of a larger source of light bounded by a straight edge parallel to that of the screen at the observing end, and of a small telescope to assist the eye. Worthy of notice is a recent application by R. Cheshire§ to determine with considerable precision for practical purposes the refractive index of irregular glass fragments. When the fragment is surrounded by liquid|| of slightly different index contained in a suitable tank, it appears luminous as an irregularity, but by adjusting the composition of the liquid it may be made to disappear. The indices are then equal, and that of the liquid may be determined by more usual methods.

We have seen that according to geometrical optics ($\lambda = 0$)

* *Ann. de l'Observ. de Paris*, t. v. Collected Memoirs, Paris, 1878.

† 'Smithsonian Contribution to Knowledge,' Jan. 1864.

‡ Pogg. *Ann.* Bd. cxxviii. p. 126 (1866); Bd. cxxxi. pp. 33, 180 (1867).

§ *Phil. Mag.* vol. xxxii. p. 409 (1916).

|| The liquid employed was a solution of mercuric iodide, and is spoken of as Thoulet's solution. Liveing (*Camb. Phil. Proc.* vol. iii. p. 258, 1879), who made determinations of the dispersive power, refers to Sonstadt (*Chem. News*, vol. xxix. p. 128, 1874). I do not know the date of Thoulet's use of the solution, but suspect that it was subsequent to Sonstadt's.

the regular light from an infinitely fine slit may be cut off suddenly, and that an irregularity will become apparent in full brightness however little (in the right direction) it may deflect the proper course of the rays. In considering the limits of sensibility we must remember that with a finite λ the image of the slit cannot be infinitely narrow, but constitutes a diffraction pattern of finite size. If we suppose the aperture bounding the field of view to be rectangular, we may take the problem to be in two dimensions, and the image consists of a central band of varying brightness bounded by dark edges and accompanied laterally by successions of bands of diminishing brightness. A screen whose edge is at the geometrical focus can cut off only half the light and, even if the lateral bands could be neglected altogether, it must be further advanced through half the width of the central band before the field can become dark. The width of the central band depends upon the horizontal aperture a (measured perpendicularly to the slit supposed vertical), the distance f between the lens and the screen, and the wave-length λ . By elementary diffraction theory the first darkness occurs when the difference of retardations of the various secondary rays issuing from the aperture ranges over one complete wave-length, *i. e.* when the projection of the aperture on the central secondary ray is equal to λ . The half-width (ξ) of the central band is therefore expressed by $\xi = f\lambda/a$.

If a prism of relative index μ , and of small angle i , be interposed near the lens, the geometrical focus of rays passing through the prism will be displaced through a distance $(\mu-1)if$. If we identify this with ξ as expressed above, we have

$$(\mu-1)i = \lambda/a, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

as the condition that the half maximum brightness of the prism shall coincide with approximate extinction of the remainder of the field of view. If the linear aperture of the prism be b , supposed to be small in comparison with a , the maximum retardation due to it is

$$(\mu-1)ib = \lambda \cdot b/a; \quad . \quad . \quad . \quad . \quad . \quad (2)$$

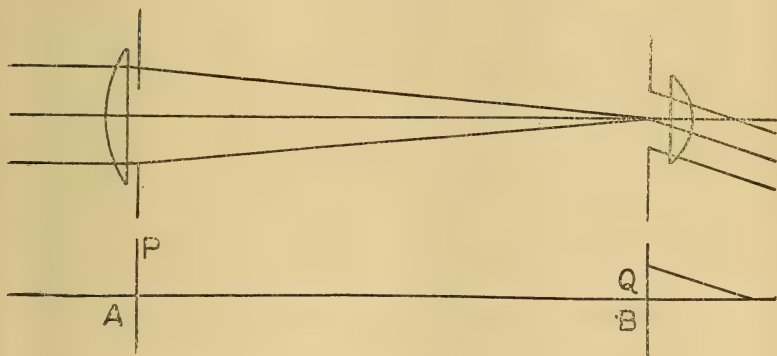
and we recognize that easy visibility of the prism on the darkened field is consistent with a maximum retardation which is a small fraction of λ .

In Cheshire's application of Foucault's method (for I think it should be named after him) the prism had an angle i of 10° , and the aperture a was 8 cms., although it would

appear from the sketch that the whole of it was not used. Thus in (1) λ/ia would be about 5×10^{-5} ; and the accuracy with which μ was determined (about ± 0.00002) is of the order that might be expected.

It is of interest to trace further and more generally what the wave theory has to tell us, still supposing that the source of light is from an infinitely narrow slit (or, what comes to the same, a slit of finite width at an infinite distance), and that the apertures are rectangular. The problem may then be supposed to be in two dimensions*, although in strictness this requires that the elementary sources distributed uniformly along the length of the slit should be all in one phase. The calculation makes the usual assumption, which cannot be strictly true, that the effect of a screen is merely to stop those parts of the wave which impinge upon it, without influencing the neighbouring parts. In fig. 1, A represents

Fig. 1.



the lens with its rectangular aperture, which brings parallel rays to a focus. In the focal plane B are two adjustable screens with vertical edges, and immediately behind is the eye or objective of a small telescope. The rays from the various points Q of the second aperture, which unite at a point in the focal plane of the telescope, or of the retina, may be regarded as a parallel pencil inclined to the axis at a small angle ϕ . P is a point in the first aperture, $AP = x$, $BQ = \xi$, $AB = f$. Any additional linear retardation operative at A may be denoted by R, a function of x . Thus if V be the velocity of propagation and $\kappa = 2\pi/\lambda$, the vibration at the

* Compare *Wave Theory*, Encyc. Brit. 1888; 'Scientific Papers,' vol. iii. p. 84.

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point ξ of the second aperture will be represented by

$$\int dx \sin \kappa \left(Vt - f - R + \frac{x\xi}{f} \right),$$

or, if $x/f = \theta$, by

$$\int d\theta \sin \kappa (Vt - f - R + \theta\xi), \dots \dots \dots (3)$$

the limits for θ corresponding to the angular aperture of the lens A. For shortness we shall omit κ^* , which can always be restored on considering "dimensions," and shall further suppose that R is at most a linear function of θ , say $\rho + \sigma\theta$, or, at any rate, that the whole aperture can be divided into parts for each of which R is a linear function. In the former case the constant part ρ may be associated with $Vt - f$, and if T be written for $Vt - f - \rho$, (3) becomes

$$\sin T \int d\theta \cos (\xi - \sigma)\theta + \cos T \int d\theta \sin (\xi - \sigma)\theta. \dots (4)$$

Since the same values of ρ , σ apply over the whole aperture, the range of integration is between $\pm\theta$, where θ denotes the angular semi-aperture, and then the second term, involving $\cos T$, disappears, while the effect of σ is represented by a shift in the origin of ξ , as was to be expected. There is now no real loss of generality in omitting R altogether, so that (4) becomes simply

$$2 \sin T \frac{\sin \xi\theta}{\xi}, \dots \dots \dots (5)$$

as in the usual theory. The borders of the central band correspond to $\xi\theta$, or rather $\kappa\xi\theta = \pm\pi$, or $\xi\theta = \pm\frac{1}{2}\lambda$, which agrees with the formula used above, since $2\theta = a/f$.

When we proceed to inquire what is to be observed at angle ϕ we have to consider the integral

$$2 \int d\xi \sin (T + \phi\xi) \frac{\sin \theta\xi}{\xi} = \sin T \int \frac{\sin (\theta + \phi)\xi + \sin (\theta - \phi)\xi}{\xi} d\xi \\ + \cos T \int \frac{\cos (\theta - \phi)\xi - \cos (\theta + \phi)\xi}{\xi} d\xi. \dots (6)$$

It will be observed that, whatever may be the limits for ξ , the first integral is an even and the second an odd function of ϕ , so that the intensity (I), represented by the sum of the squares of the integrals, is an even function. The field of view is thus symmetrical with respect to the axis.

* Equivalent to supposing $\lambda = 2\pi$.

The integrals in (6) may be at once expressed in terms of the so-called sine-integral and cosine-integral defined by

$$\text{Si}(x) = \int_0^x \frac{\sin x}{x} dx, \quad \text{Ci}(x) = \int_{\infty}^x \frac{\cos x}{x} dx.$$

If the limits of ξ be ξ_1 and ξ_2 we get

$$\begin{aligned} & \sin T[\text{Si}\{(\theta + \phi)\xi_2\} - \text{Si}\{(\theta + \phi)\xi_1\} \\ & \quad + \text{Si}\{(\theta - \phi)\xi_2\} - \text{Si}\{(\theta - \phi)\xi_1\}] \\ & + \cos T[\text{Ci}\{(\theta - \phi)\xi_2\} - \text{Ci}\{(\theta - \phi)\xi_1\} \\ & \quad - \text{Ci}\{(\theta + \phi)\xi_2\} + \text{Ci}\{(\theta + \phi)\xi_1\}]. \quad (7) \end{aligned}$$

If $\xi_1 = -\xi_2 = -\xi$, so that the second aperture is symmetrical with respect to the axis, the Ci's, being even functions, disappear, and we have simply

$$2 \sin T[\text{Si}\{(\theta + \phi)\xi\} + \text{Si}\{(\theta - \phi)\xi\}] \quad . \quad . \quad . \quad (8)$$

If the aperture of the telescope be not purposely limited, the value of ξ , or rather of $\kappa\xi$, is very great, and for most purposes the error will be small in supposing it infinite. Now $\text{Si}(\pm\infty) = \pm\frac{1}{2}\pi$, so that if ϕ is numerically less than θ , $I = 4\pi^2$, but if ϕ is numerically greater than θ , $I = 0$. The angular field of view 2θ is thus uniformly illuminated and the transition to darkness at angles $\pm\theta$ is sudden—that is, the edges are seen with infinite sharpness. Of course, ξ cannot really be infinite, nor consequently the resolving power of the telescope; but we may say that the edges are defined with full sharpness. The question here is the same as that formerly raised under the title “An Optical Paradox”*, the paradox consisting in the full definition of the edges of the first aperture, although nearly the whole of the light at the second aperture is concentrated in a very narrow band, which might appear to preclude more than a very feeble resolving power.

It may be well at this stage to examine more closely what is actually the distribution of light between the central and lateral bands in the diffraction pattern formed at the plane of the second aperture. By (5) the intensity of light at ξ is proportional to $\xi^{-2} \sin^2 \theta\xi$ or, if we write η for $\theta\xi$, to $\eta^{-2} \sin^2 \eta$. The whole light between 0 and η is thus

* Phil. Mag. vol. ix. p. 779 (1905); ‘Scientific Papers,’ vol. v. p. 254.

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 represented by

$$J = \int_0^{\eta} \frac{\sin^2 \eta}{\eta^2} d\eta. \quad . \quad . \quad . \quad . \quad . \quad (9)$$

J can be expressed by means of the Si-function. As may be
 verified by differentiation,

$$J = \text{Si}(2\eta) - \eta^{-1} \sin^2 \eta, \quad . \quad . \quad . \quad . \quad (10)$$

vanishing when $\eta = 0$. The places of zero illumination are
 defined by $\eta = n\pi$, when $n = 1, 2, 3$, &c.; and, if η assume one
 of these values, we have simply

$$J = \text{Si}(2\eta) = \text{Si}(2n\pi). \quad . \quad . \quad . \quad . \quad (11)$$

Thus, setting $n = 1$, we find for half the light in the central
 band

$$J = \text{Si}(2\pi) = \frac{1}{2}\pi - \cdot 15264.$$

On the same scale half the whole light is $\text{Si}(\infty)$, or $\frac{1}{2}\pi$, so
 that the fraction of the whole light to be found in the central
 band is

$$1 - \frac{2 \times \cdot 15264}{\pi} = 1 - \cdot 097174, \quad . \quad . \quad . \quad (12)$$

or more than nine-tenths. About half the remainder is
 accounted for by the light in the two lateral bands imme-
 diately adjacent (on the two sides) to the central band.

We are now in a position to calculate the appearance of the
 field when the second aperture is actually limited by screens,
 so as to allow only the passage of the central band of the
 diffraction pattern. For this purpose we have merely to
 suppose in (8) that $\theta\xi = \pi$. The intensity at angle ϕ is thus

$$4 \left[\text{Si} \left(\frac{\theta + \phi}{\theta} \pi \right) + \text{Si} \left(\frac{\theta - \phi}{\theta} \pi \right) \right]^2. \quad . \quad . \quad (13)$$

The further calculation requires a knowledge of the function
 Si, and a little later we shall need the second function Ci.
 In ascending series

$$\text{Si}(x) = x - \frac{1}{3} \frac{x^3}{1 \cdot 2 \cdot 3} + \frac{1}{5} \frac{x^5}{1 \cdot 2 \cdot 3 \cdot 4 \cdot 5} - \frac{1}{7} \frac{x^7}{1 \cdot 2 \dots 7} + \dots \quad (14)$$

$$\text{Ci}(x) = \gamma + \frac{1}{2} \log(x^2) - \frac{1}{2} \frac{x^2}{1 \cdot 2} + \frac{1}{4} \frac{x^4}{1 \cdot 2 \cdot 3 \cdot 4} - \dots; \quad (15)$$

γ is Euler's constant $\cdot 5772156$, and the logarithm is to base e .
 These series are always convergent and are practically

available when x is moderate. When x is great, we may use the semi-convergent series

$$\begin{aligned} \text{Si}(x) = & \frac{\pi}{2} - \cos x \left\{ \frac{1}{x} - \frac{1 \cdot 2}{x^3} + \frac{1 \cdot 2 \cdot 3 \cdot 4}{x^5} - \frac{1 \cdot 2 \dots 6}{x^7} + \dots \right\} \\ & - \sin x \left\{ \frac{1}{x^2} - \frac{1 \cdot 2 \cdot 3}{x^4} + \frac{1 \cdot 2 \cdot 3 \cdot 4 \cdot 5}{x^6} - \dots \right\}, \quad (16) \end{aligned}$$

$$\begin{aligned} \text{Ci}(x) = & \sin x \left\{ \frac{1}{x} - \frac{1 \cdot 2}{x^3} + \frac{1 \cdot 2 \cdot 3 \cdot 4}{x^5} - \dots \right\} \\ & - \cos x \left\{ \frac{1}{x^2} - \frac{1 \cdot 2 \cdot 3}{x^4} + \frac{1 \cdot 2 \cdot 3 \cdot 4 \cdot 5}{x^6} - \dots \right\}. \quad (17) \end{aligned}$$

Tables of the functions have been calculated by Glaisher*. For our present purpose it would have been more convenient had the argument been πx , rather than x . Between $x=5$ and $x=15$, the values of $\text{Si}(x)$ are given for integers only, and interpolation is not effective. For this reason some values of ϕ/θ are chosen which make $(1 + \phi/\theta)\pi$ integral. The calculations recorded in Table I. refer in the first instance to the values of

$$\text{Si}(1 + \phi/\theta)\pi + \text{Si}(1 - \phi/\theta)\pi. \quad (18)$$

TABLE I.

$$\kappa \theta \xi_1 = -\pi, \quad \kappa \theta \xi_2 = +\pi.$$

| $\phi/\theta.$ | (18). | (18) ² . |
|----------------|--------|---------------------|
| 0.0000 | 3.704 | 13.72 |
| 0.2732 | 3.475 | 12.08 |
| 0.5000 | 2.979 | 8.87 |
| 0.5915 | 2.721 | 7.40 |
| 0.9099 | 1.707 | 2.91 |
| 1.0000 | 1.418 | 2.01 |
| 1.2282 | 0.758 | 0.57 |
| 1.5465 | 0.115 | 0.01 |
| 2.0000 | -0.177 | 0.03 |

It will be seen that, in spite of the fact that nine-tenths of the whole light passes, the definition of what should be the edge of the field at $\phi = \theta$ is very bad. Also that the illumination at $\phi = 0$ is *greater* than what it would be (π^2) if the second screening were abolished altogether ($\pm \xi = \infty$).

So far we have dealt only with cases where the second

* Phil. Trans. vol. clx. p. 367 (1870).

aperture is symmetrically situated with respect to the geometrical focus. This restriction we will now dispense with, considering first the case where $\xi_1=0$ and $\xi_2(=\xi)$ is positive and of arbitrary value. The coefficient of $\sin T$ in (7) becomes simply

$$\text{Si}\{(\theta+\phi)\xi\} + \text{Si}\{(\theta-\phi)\xi\}. \quad . \quad . \quad . \quad (19)$$

In the coefficient of $\cos T$, $\text{Ci}\{(\theta+\phi)\xi_1\}$, $\text{Ci}\{(\theta-\phi)\xi_1\}$ assume infinite values, but by (15) we see that

$$\text{Ci}\{(\theta+\phi)\xi_1\} - \text{Ci}\{(\theta-\phi)\xi_1\} = \log \left| \frac{\theta+\phi}{\theta-\phi} \right|, \quad . \quad (20)$$

so that the coefficient of $\cos T$ is

$$\text{Ci}\{(\theta-\phi)\xi\} - \text{Ci}\{(\theta+\phi)\xi\} + \log \left| \frac{\theta+\phi}{\theta-\phi} \right|. \quad . \quad (21)$$

The intensity I at angle ϕ is represented by the sum of the squares of (19) and (21). When $\phi=0$ at the centre of the field of view, $I=4(\text{Si}\theta\xi)^2$, but at the edges for which it suffices to suppose $\phi=+\theta$, a modification is called for, since $\text{Ci}\{(\theta-\phi)\xi\}$ must then be replaced by $\gamma + \log |(\theta-\phi)\xi|$. Under these circumstances the coefficient of $\cos T$ becomes

$$\gamma + \log (2\theta\xi) - \text{Ci}(2\theta\xi),$$

and

$$I = \{\text{Si}(2\theta\xi)\}^2 + \{\gamma + \log (2\theta\xi) - \text{Ci}(2\theta\xi)\}^2. \quad . \quad (22)$$

If in (22) ξ be supposed to increase without limit, we find

$$I = \frac{1}{4}\pi^2 + \{\log \theta\xi\}^2, \quad . \quad . \quad . \quad (23)$$

becoming logarithmically infinite.

Since in practice ξ , or rather $\kappa\xi$, is large, the edges of the field may be expected to appear very bright.

As may be anticipated, this conclusion does not depend upon our supposition that $\xi_1=0$. Reverting to (7) and supposing $\phi=\theta$, we have

$$\begin{aligned} & \sin T [\text{Si}(2\theta\xi_2) - \text{Si}(2\theta\xi_1)] \\ & + \cos T [\text{Ci}(2\theta\xi_1) - \text{Ci}(2\theta\xi_2) + \log (\xi_2/\xi_1)], \quad . \quad (24) \end{aligned}$$

and $I=\infty$, when $\xi_2=\infty$. If ξ_1 vanishes in (24), we have only to replace $\text{Ci}(2\theta\xi_1)$ by $\gamma + \log (2\theta\xi_1)$ in order to recover (22).

We may perhaps better understand the abnormal increase of illumination at the edges of the field by a comparison with the familiar action of a grating in forming diffraction

spectra. Referring to (5) we see that if positive values of ξ be alone regarded, the vibration in the place of the second aperture, represented by $\xi^{-1} \sin(\theta\xi)$, is the same in respect of phase as would be due to a theoretically simple grating receiving a parallel beam perpendicularly, and the directions $\phi = \pm\theta$ are those of the resulting lateral spectra of the first order. On account, however, of the factor ξ^{-1} , the case differs somewhat from that of the simple grating, but not enough to prevent the illumination becoming logarithmically infinite with infinite aperture. But the approximate resemblance to a simple grating fails when we include negative as well as positive values of ξ , since there is then a reversal of phase in passing zero. Compare fig. 2, where positive

Fig. 2.



values are represented by full lines and negative by dotted lines. If the aperture is symmetrically bounded, the parts at a distance from the centre tend to compensate one another, and the intensity at $\phi = \pm\theta$ does not become infinite with the aperture.

We now proceed to consider the actual calculation of $I = (19)^2 + (21)^2$ for various values of ϕ/θ , which we may suppose to be always positive, since I is independent of the sign of ϕ . When $\xi\theta$ is very great and ϕ/θ is not nearly equal to unity, $\text{Si}\{(\theta + \phi)\xi\}$ in (19) may be replaced by $\frac{1}{2}\pi$ and $\text{Si}\{(\theta - \phi)\xi\}$ by $\pm\frac{1}{2}\pi$, according as ϕ/θ is less or greater than unity. Under the same conditions the Ci's in (21) may be omitted, so that

$$I = \pi^2(1, \text{ or } 0) + \left\{ \log \left| \frac{\theta + \phi}{\theta - \phi} \right| \right\}^2 . . . (25)$$

But if we wish to avoid the infinity when $\phi = \theta$, we must make some supposition as to the actual value of $\theta\xi$, or rather of $2\pi\theta\xi/\lambda$. In some observations to be described later $a = 1$ inch, $\xi = \frac{1}{2}$ inch, $1/\lambda = 40,000$, and $\theta = \frac{1}{2}a/f$. Also f was about 10 feet = 120 inches. For simplicity we may suppose $f = 40\pi$, so that $2\pi\theta\xi/\lambda = 500$, or in our usual

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notation $\theta\xi=500$. Thus

$$(19) = \text{Si}\{500(1 + \phi/\theta)\} + \text{Si}\{500(1 - \phi/\theta)\}, \quad . \quad (26)$$

and

$$(21) = \text{Ci}\{500(1 - \phi/\theta)\} - \text{Ci}\{500(1 + \phi/\theta)\} \\ + \log(1 + \phi/\theta) - \log|1 - \phi/\theta| \quad . \quad . \quad (27)$$

For the purposes of a somewhat rough estimate we may neglect the second Ci in (27) and identify the first Si in (26) with $\frac{1}{2}\pi$ for all (positive) values of ϕ/θ . Thus when $\phi=0$, $I=\pi^2$; and when $\phi=\infty$, $I=0$.

When $\phi/\theta=1$, we take

$$(26) = \frac{1}{2}\pi = 1.571, \quad (26)^2 = 2.467.$$

In (27)

$$\text{Ci}\{500(1 - \phi/\theta)\} = \gamma + \log 500 + \log(1 - \phi/\theta),$$

so that

$$(27) = \gamma + \log 1000 = 7.485, \quad (27)^2 = 56.03;$$

and

$$I = 58.50.$$

For the values of ϕ/θ in the neighbourhood of unity we may make similar calculations with the aid of Glaisher's Tables. For example, if $\phi/\theta = 1 \mp .02$, we have

$$500(1 - \phi/\theta) = \pm 10.$$

From the Tables

$$\text{Si}(\pm 10) = \pm 1.6583, \quad \text{Ci}(\pm 10) = -.0455,$$

and thence

$$I(.98) = 31.13, \quad I(1.02) = 20.89.$$

As regards values of the argument outside these units, we may remark that when x exceeds 10, $\text{Si}(x) - \frac{1}{2}\pi$ and $\text{Ci}(x)$ are approximately periodic in period 2π and of order x^{-1} . It is hardly worth while to include these fluctuations, which would manifest themselves as rather feeble and narrow bands, superposed upon the general ground, and we may thus content ourselves with (25). If we apply this to ± 10 , we get

$$I(.98) = 30.98, \quad I(1.02) = 21.30;$$

and the smoothed values differ but little from those calculated for ± 10 more precisely. The Table (II.) annexed shows the values of I for various values of ϕ/θ . Those in the 2nd and 8th columns are smoothed values as explained, and they would remain undisturbed if the value of $\theta\xi$ were increased. It will be seen that the maximum illumination near the edges is some 6 times that at the centre.

TABLE II.

$$\kappa\theta\xi_1=0, \quad \kappa\theta\xi_2=500.$$

| $\phi/\theta.$ | I. | $\phi/\theta.$ | I. | $\phi/\theta.$ | I. | $\phi/\theta.$ | I. |
|----------------|-------|----------------|-------|----------------|-------|----------------|-------|
| 0·000 | 9·87 | 0·980 | 31·13 | 1·001 | 56·28 | 1·05 | 13·76 |
| 0·250 | 10·13 | 0·990 | 35·78 | 1·002 | 52·89 | 1·10 | 9·24 |
| 0·500 | 11·08 | 0·992 | 39·98 | 1·004 | 44·09 | 1·20 | 5·76 |
| 0·800 | 14·71 | 0·994 | 46·81 | 1·006 | 35·27 | 1·50 | 2·59 |
| 0·900 | 18·51 | 0·996 | 54·13 | 1·008 | 29·03 | 2·00 | 1·21 |
| 0·950 | 23·27 | 0·998 | 58·81 | 1·010 | 26·14 | ∞ | 0 |
| | | 0·999 | 59·36 | 1·020 | 20·89 | | |
| | | 1·000 | 58·50 | | | | |

TABLE III.

$$\kappa\theta\xi_1=\pi, \quad \kappa\theta\xi_2=500.$$

| $\phi/\theta.$ | I. | $\phi/\theta.$ | I. |
|----------------|-------|----------------|------|
| 0·00 | 0·32 | 1·01 | 8·98 |
| 0·50 | 0·48 | 1·02 | 6·57 |
| 0·91 | 2·46 | 1·23 | 0·58 |
| 0·98 | 7·55 | 1·55 | 0·13 |
| 0·99 | 9·90 | 1·86 | 0·05 |
| 1·00 | 25·51 | ∞ | 0·00 |

In the practical use of Foucault's method the general field would be darkened much more than has been supposed above where half the whole light passes. We may suppose that the screening just cuts off the central band, as well as all on one side of it, so that $\theta\xi_1=\pi$. In this case (7) becomes

$$\begin{aligned} & \sin T[\text{Si}(\theta+\phi)\xi + \text{Si}(\theta-\phi)\xi - \text{Si}(1+\phi/\theta)\pi - \text{Si}(1-\phi/\theta)\pi] \\ & + \cos T[\text{Ci}(\theta-\phi)\xi - \text{Ci}(\theta+\phi)\xi + \text{Ci}(1+\phi/\theta)\pi \\ & \quad - \text{Ci}(1-\phi/\theta)\pi]. \dots \quad (28) \end{aligned}$$

We will apply it to the case already considered, where $\theta\xi=500$, as before omitting $\text{Ci}(\theta+\phi)\xi$ and equating $\text{Si}(\theta+\phi)\xi$ to $\frac{1}{2}\pi$. Thus

$$\begin{aligned} I = & [\tfrac{1}{2}\pi + \text{Si } 500(1-\phi/\theta) - \text{Si}(1+\phi/\theta)\pi - \text{Si}(1-\phi/\theta)\pi]^2 \\ & + [\text{Ci } 500(1-\phi/\theta) + \text{Ci}(1+\phi/\theta)\pi - \text{Ci}(1-\phi/\theta)\pi]^2. \quad (29) \end{aligned}$$

When $\phi = \infty$, $I = 0$. When $\phi = 0$,

$$I = [\pi - 2\text{Si}\pi]^2 = \cdot 3162.$$

When $\phi = \theta$,

$$I = [\tfrac{1}{2}\pi - \text{Si}(2\pi)]^2 + [\log(500/\pi) + \text{Ci}(2\pi)]^2 = 25\cdot 51;$$

so that the brightness of the edges is now about 80 times that at the centre of the field. The remaining values of I in Table III. have been calculated as before with omission of the terms representing minor periodic fluctuations.

Hitherto we have treated various kinds of screening, but without additional retardation at the plane of the first aperture. The introduction of such retardation is, of course, a complication, but in principle it gives rise to no difficulty, provided the retardation be linear in θ over the various parts of the aperture. The final illumination as a function of ϕ can always be expressed by means of the Si- and Ci-functions.

As the simplest case which presents something essentially novel, we may suppose that an otherwise constant retardation (R) changes sign when $\theta = 0$, is equal (say) to $+\rho$ when θ is positive and to $-\rho$ when θ is negative. Then (3) becomes

$$\begin{aligned} \int_{-\theta}^0 \sin(T + \rho + \theta\xi) d\theta + \int_0^{\theta} \sin(T - \rho + \theta\xi) d\theta \\ = 2 \sin T \left[\cos \rho \frac{\sin \theta\xi}{\xi} + \sin \rho \frac{1 - \cos \theta\xi}{\xi} \right], \quad (30) \end{aligned}$$

reducing to (5) when $\rho = 0$. This gives the vibration at the point ξ of the second aperture. If $\xi = 0$, (30) becomes $2\theta \cos \rho \sin T$, and vanishes when $\cos \rho = 0$, for instance, when the whole difference of retardation $2\rho = \pi$, or (reckoned in wave-lengths) $\frac{1}{2}\lambda$.

The vibration in direction ϕ behind the second aperture is to be obtained by writing $T + \phi\xi$ for T in (30) and integrating with respect to ξ . This gives

$$\begin{aligned} 2 \sin T \int d\xi \cos \phi\xi \left\{ \cos \rho \frac{\sin \theta\xi}{\xi} + \sin \rho \frac{1 - \cos \theta\xi}{\xi} \right\} \\ + 2 \cos T \int d\xi \sin \phi\xi \left\{ \cos \rho \frac{\sin \theta\xi}{\xi} + \sin \rho \frac{1 - \cos \theta\xi}{\xi} \right\}, \quad (31) \end{aligned}$$

and the illumination (I) is independent of the sign of ϕ , which we may henceforward suppose to be positive.

If the second aperture be symmetrically placed, we may

take the limits to be expressed as $\pm \xi$, and (31) becomes

$$2 \sin T \cos \rho \int_0^{\xi} \frac{\sin (\theta + \phi) \xi + \sin (\theta - \phi) \xi}{\xi} d\xi \\ + 2 \cos T \sin \rho \int_0^{\xi} \frac{2 \sin \phi \xi - \sin (\theta + \phi) \xi + \sin (\theta - \phi) \xi}{\xi} d\xi. \quad (32)$$

If we apply this to $\xi = \infty$ to find what occurs when there is no screening, we fall upon ambiguities, for (32) becomes

$$2 \sin T \cos \rho \left\{ \frac{1}{2} \pi \pm \frac{1}{2} \pi \right\} + 2 \cos T \sin \rho \left\{ 2 \text{Si}(\phi \xi) - \frac{1}{2} \pi \pm \frac{1}{2} \pi \right\},$$

the alternatives following the sign of $\theta - \phi$, with exclusion of the case $\phi = \theta$. If ϕ is finite, $2 \text{Si}(\phi \xi)$ may be equated to π , and we get

$$I = 4\pi^2 (1 \text{ or } 0),$$

according as $\theta - \phi$ is positive or negative. But if $\phi = 0$ absolutely, $\text{Si}(\phi \xi)$ disappears, however great ξ may be; and when ϕ is small,

$$I = 4\pi^2 \cos^2 \rho + 4 \sin^2 \rho \{ 2 \text{Si}(\phi \xi) \}^2,$$

in which the value of the second term is uncertain, unless indeed $\sin \rho = 0$.

It would seem that the difficulty depends upon the assumed discontinuity of R when $\theta = 0$. If the limits for θ be $\pm \alpha$ (up to the present written as $\pm \theta$), what we have to consider is

$$\int_{-\infty}^{+\infty} d\xi \left[\int_{-\alpha}^{+\alpha} d\theta \sin \{ T - R + (\theta + \phi) \xi \} \right],$$

in which hitherto we have taken first the integration with respect to θ . We propose now to take first the integration with respect to ξ , introducing the factor $e^{\pm \mu \xi}$ to ensure convergency. We get

$$2 \sin (T - R) \int_0^{\infty} e^{-\mu \xi} \cos (\theta + \phi) \xi \cdot d\xi = \frac{2\mu \sin (T - R)}{\mu^2 + (\theta + \phi)^2}. \quad (33)$$

There remains the integration with respect to θ , of which R is supposed to be a continuous function. As μ tends to vanish, the only values of θ which contribute are confined more and more to the neighbourhood of $-\phi$, so that ultimately we may suppose θ to have this value in R . And

$$\int_{-\alpha}^{+\alpha} \frac{\mu d\theta}{\mu^2 + (\theta + \phi)^2} = \tan^{-1} \frac{\phi + \alpha}{\mu} - \tan^{-1} \frac{\phi - \alpha}{\mu},$$

which is π , if ϕ lies between $\pm \alpha$, and 0 if ϕ lies outside these limits, when μ is made vanishing small. The intensity

in any direction ϕ is thus independent of R altogether. This procedure would fail if R were discontinuous for any values of θ .

Resuming the suppositions of equation (31), let us now further suppose that the aperture extends from ξ_1 to ξ_2 , where both ξ_1 and ξ_2 are positive and $\xi_2 > \xi_1$. Our expression for the vibration in direction ϕ becomes

$$\begin{aligned} & \sin T [\cos \rho \{ \text{Si}(\theta + \phi)\xi + \text{Si}(\theta - \phi)\xi \} \\ & \quad + \sin \rho \{ 2\text{Ci}(\phi\xi) - \text{Ci}(\theta + \phi)\xi - \text{Ci}(\theta - \phi)\xi \}]_{\xi_1}^{\xi_2} \\ & + \cos T [\cos \rho \{ \text{Ci}(\theta - \phi)\xi - \text{Ci}(\theta + \phi)\xi \} \\ & \quad + \sin \rho \{ 2\text{Si}(\phi\xi) - \text{Si}(\theta + \phi)\xi + \text{Si}(\theta - \phi)\xi \}]_{\xi_1}^{\xi_2}. \quad (34) \end{aligned}$$

We will apply this to the case already considered where $\xi_2\theta = 500$, $\xi_1\theta = \pi$; and since we are now concerned mainly with what occurs in the neighbourhood of $\phi = 0$, we may confine ϕ to lie between the limits 0 and $\frac{1}{2}\theta$. Under these circumstances, and putting minor rapid fluctuations out of account, we may neglect $\text{Ci}(\theta \pm \phi)\xi_2$ and equate $\text{Si}(\theta \pm \phi)\xi_2$ to $\frac{1}{2}\pi$. A similar simplification is admissible for $\text{Si}(\phi\xi_2)$, $\text{Ci}(\phi\xi_2)$, unless ϕ/θ is very small.

When $\phi = 0$, (34) gives

$$\sin T [\cos \rho \{ \pi - 2\text{Si}(\pi) \} + \sin \rho \{ 2 \log (500/\pi) + 2\text{Ci}(\pi) \}],$$

in which

$$\pi - 2\text{Si}(\pi) = -\cdot 5623, \quad \text{Ci}(\pi) = \cdot 0738, \quad \log (500/\pi) = 5\cdot 0699.$$

Thus for the intensity

$$I(0) = [-\cdot 5623 \cos \rho + 10\cdot 2874 \sin \rho]^2. \quad (35)$$

If $\rho = 0$, we fall back upon a former result (3162). If $\rho = \frac{1}{4}\pi$, $I(0) = 47\cdot 3$.

Interest attaches mainly to small values of ρ , and we see that the effect depends upon the sign of ρ . A positive ρ means that the retardation at the first aperture takes place on the side opposite to that covered by the screen at the second aperture. As regards magnitude, we must remember that ρ stands for an angular retardation $\kappa\rho$, or $2\pi\rho/\lambda$; so that, for example, $\rho = \frac{1}{4}\pi$ above represents a linear retardation $\lambda/8$, and a total relative retardation between the two halves of the first aperture equal to $\lambda/4$.

The second column of Table IV. gives the general expression for the vibration in terms of ρ for various values of ϕ/θ , followed by the values of the intensity (I) for $\sin \rho = \pm 1/10$ and $\sin \rho = \pm 1/\sqrt{2}$.

TABLE IV.

$$\kappa\theta\xi_1=\pi, \quad \kappa\theta\xi_2=500.$$

| $\frac{\phi}{\theta}$ | Formula for Vibration. | I. | | I. | |
|-----------------------|--|--------------|------|--------------|--------|
| | | sin ρ . | | sin ρ . | |
| | | +1. | -1. | +1/√2. | -1/√2. |
| 0 | $\sin T\{-\cdot56 \cos \rho + 10\cdot29 \sin \rho\}$ | ·22 | 2·53 | 47·3 | 58·9 |
| ·001 | $\sin T\{-\cdot56 \cos \rho + 10\cdot16 \sin \rho\}$ + $\cos T \times \cdot99 \sin \rho$ | ·22 | 2·50 | 46·6 | 58·0 |
| ·010 | $\sin T\{-\cdot56 \cos \rho + 5\cdot53 \sin \rho\}$ + $\cos T \times 3\cdot10 \sin \rho$ | ·10 | 1·34 | 17·2 | 23·4 |
| ·050 | $\sin T\{-\cdot55 \cos \rho + 2\cdot71 \sin \rho\}$ + $\cos T\{-\cdot10 \cos \rho + 2\cdot83 \sin \rho\}$ | ·11 | ·83 | 6·0 | 9·6 |
| ·100 | $\sin T\{-\cdot53 \cos \rho + 1\cdot37 \sin \rho\}$ + $\cos T\{-\cdot20 \cos \rho + 2\cdot52 \sin \rho\}$ | ·16 | ·66 | 3·0 | 5·5 |
| ·250 | $\sin T\{-\cdot37 \cos \rho - \cdot17 \sin \rho\}$ + $\cos T\{-\cdot46 \cos \rho + 1\cdot66 \sin \rho\}$ | ·23 | ·52 | ·86 | 2·3 |
| ·500 | $\sin T\{+\cdot16 \cos \rho - \cdot67 \sin \rho\}$ + $\cos T\{-\cdot67 \cos \rho + \cdot64 \sin \rho\}$ | ·38 | ·59 | ·13 | 1·2 |

It will be seen that the direction of the discontinuity ($\phi=0$) is strongly marked by excess of brightness, and that especially when ρ is small there is a large variation with the sign of ρ .

Perhaps the next case in order of simplicity of a variable R is to suppose $R=0$ from $\theta=-\theta$ to $\theta=0$, and $R=\sigma\theta$ from $\theta=0$ to $\theta=+\theta$, corresponding to the introduction of a prism of small angle, whose edge divides equally the field of view. For the vibration in the focal plane we get

$$\begin{aligned} & \sin T \left[\frac{\sin \theta \xi}{\xi} + \frac{\sin (\xi - \sigma)\theta}{\xi - \sigma} \right] \\ & + \cos T \left[\frac{1 - \cos (\xi - \sigma)\theta}{\xi - \sigma} - \frac{1 - \cos \xi \theta}{\xi} \right]. \quad (36) \end{aligned}$$

In order to find what would be seen in direction ϕ , we should have next to write $(T + \phi\xi)$ for T and integrate again with respect to ξ between the appropriate limits. As to this there is no difficulty, but the expressions are rather long. It may suffice to notice that whatever the limits may be, no infinity enters at $\phi=0$, in which case we have merely to integrate (36) as it stands. For although the denominators

become zero when $\xi=0$ or $\xi=\sigma$, the four fractions themselves always remain finite. The line of transition between the two halves of the field is not so marked as when there was an actual discontinuity in the retardation itself.

In connexion with these calculations I have made for my own satisfaction a few observations, mainly to examine the enhanced brightness at the edges of the field of view. The luminous border is shown in Draper's drawing, and is described by Töpler as due to diffraction. The slit and focussing lens were those of an ordinary spectroscope, the slit being drawn back from the "collimating" lens. The telescope was from the same instrument, now mounted independently at a distance so as to receive an image of the slit and itself focussed upon the first lens. The rectangular aperture at the first lens was originally cut out of the black card. The principal dimensions have already been given. A flat paraffin-flame afforded sufficient illumination. The screens used in front of the telescope were razor-blades (Gillettes), and were adjusted in position with the aid of an eyepiece, the telescope being temporarily removed. It is not pretended that the arrangements used corresponded fully to the suppositions of theory.

The brightness of the vertical edge of the field of view is very conspicuous when the light is partly cut off by the advancing screen. A question may arise as to how much of it may be due to light ordinarily reflected at the edges of the first aperture. With the aperture cut in cardboard, I think this part was appreciable, but the substitution of a razor-edge at the first aperture made no important difference. The strongly illuminated border must often have been seen in repetitions of Foucault's experiment, but I am not aware that it has been explained.

To examine the sudden transition from one uniform retardation to another, I used a piece of plate glass which had been etched in alternate strips with hydrofluoric acid to a depth of about $\frac{1}{4}\lambda$ *. When this was set up in front of the first aperture with strips vertical, the division-lines shone out brightly, when the intervening areas were uniformly dark or nearly so. No marked difference was seen between the alternate division-lines corresponding to opposite signs of ρ . Perhaps this could hardly be expected. The whole relative retardation, reckoned as a distance, is $\frac{1}{8}\lambda$, and is thus intermediate between the values specified in Table IV. It would be of interest to make a similar experiment with a shallower etching.

Terling Place, Witham.

Jan. 5, 1917.

* Compare 'Nature,' vol. lxiv. p. 385 (1901); 'Scientific Papers' vol. iv. pp. 546, 547.

XIII. *On Unipolar Induction: Another Experiment and its Significance as Evidence for the Existence of the Æther.*
By E. H. KENNARD, *Ph.D.**

§ 1. *Introduction.*

“UNIPOLAR induction in the general sense may be defined as induction due to motion alone.” This condition requires that the magnetic induction shall remain constant at all points fixed relative to any part of the material system involved, so as to exclude any possible effects due to a changing magnetic field; and the only form of motion satisfying this requirement is rotation about an axis of magnetic symmetry. The fundamental problem of unipolar induction is therefore this, whether the induced E.M.F. is determined by the absolute rotation of the system or by the rotation of its parts relative to each other.

Theory has answered the question in three principal ways. The oldest view, put forward by Faraday and adopted by Lorentz, refers the effects to an induced electromotive intensity given by

$$\frac{1}{c}[v \times B],$$

where B =magnetic induction and v =velocity relative to the æther (assumed stationary); the effect will therefore depend in part upon the rotation of the system as a whole. The “moving line” theory adopts the same expression, but interprets v as velocity relative to axes fixed in the material magnetic system; this view is virtually included in Neumann’s theory of electromagnetism, and is based upon complete relativity, so that the effects depend only upon relative rotation between the parts.

Experimentally, the question can be answered only by observations upon open circuits. The first investigation of this kind seems to be one made by the author †, in which an iron bar magnetized by a stationary solenoid was set in rotation inside an insulated metal cylinder connected to earth, and a charge was looked for on the cylinder due to a possible E.M.F. in the earthing wire. The result was definitely negative. Barnett’s objection ‡ that the negative result might conceivably be due to the non-rotation of the solenoid is valid, but seems decidedly weak, for it assumes a

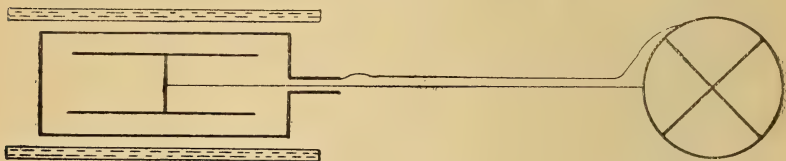
* Communicated by the Author.

† E. H. Kennard, *Phil. Mag.* June 1912, p. 937.

‡ S. J. Barnett, *Phys. Zeits.* Sept. 1, 1912, p. 803.

radical difference to exist between induced and permanent magnetism, for which there is no other evidence; it even requires that the remanent magnetism shall not acquire the inducing properties of permanent magnetism until the magnetizing force is removed, for the remanence in the bar employed amounted to over 25 per cent. This experiment serves, therefore, to throw grave doubt upon the moving-line theory; but beyond that its theoretical significance is limited by the fact that the rotating magnet was necessarily enclosed in a second metallic screen of small diameter, and this might conceivably act so as to cut off the effect.

Fig. 1.



A more instructive but more difficult arrangement consists of a cylindrical condenser inside a coaxial solenoid (fig. 1), both capable of rotation about their longitudinal axis; the condenser is connected to an electrometer as shown. Let the condenser be short-circuited and set in rotation with the solenoid energized. Then according to either Lorentz's or the moving-line theory (but not according to Hertz's) the two cylinders of the condenser should come to different potentials, and the inner one at least should be charged. According to Lorentz's theory rotation of the solenoid should have no effect upon this charge. According to the moving-line theory rotation of the solenoid alone should charge the condenser in the same manner, while the condenser should remain uncharged when condenser and solenoid rotate together with no relative motion between them.

Barnett constructed an apparatus of this sort*, and showed that rotation of the solenoid alone developed no charge upon the condenser. Later, Fehrle† reported confirmatory observations with a rather different arrangement, but his work is marred by several results which must certainly be wrong: one of his results even contradicts Faraday's law for closed circuits!

Under these circumstances, while there appeared to be little doubt of the correctness of Lorentz's theory, yet the matter

* S. J. Barnett, *Phys. Rev.* Nov. 1912, p. 323.

† Fehrle, *Ann.* xlii. p. 1109 (1913).

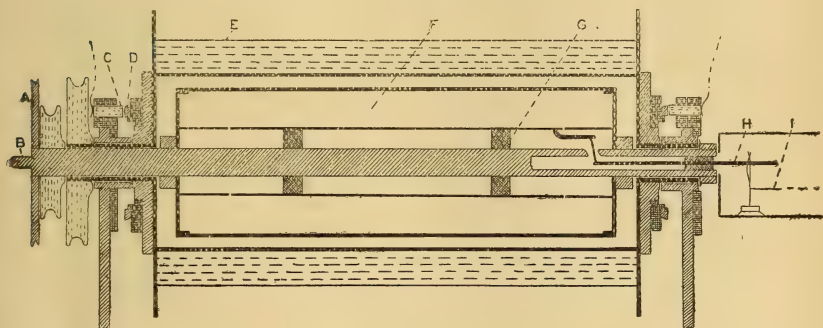
seemed of sufficient interest to justify the attempt to obtain both positive and negative results with an apparatus like that described above, and to prove experimentally that the inner cylinder really would charge up in spite of its being enclosed by a metallic screen rotating with it.

Another apparatus has accordingly been constructed in which either the condenser or the solenoid could be set in rotation. The present paper contains an account of the work and a discussion of the theoretical significance of the result.

§ 2. Apparatus.

The condenser and solenoid are shown to scale in fig. 2, which is largely self-explanatory. All metal parts, including the base, were of brass. Guard-rings in line with the inner cylinder were introduced in order to simplify the calculation. Rotation was effected by means of a belt connected to a motor placed about 2 feet away.

Fig. 2.



C, brush; D, slip-ring; E, solenoid, 22.5 cm. long, 1150 turns of wire; F, condenser: outer cylinder 20.5 cm. long, 6.64 cm. in diam.; inner cylinder 15.1 cm. long, mean diam. 1.54 cm., on amber rings G. Diam. of shaft, 1.27 cm.

The principal apparatus was earthed by a brush of brass wires sliding on the knob B, and was otherwise insulated (except for a resistance of 10,000 ohms accidentally left in place between frame and earth); the outer cylinder of the condenser is thus practically earthed at a point on the axis. In the final arrangement the needle H communicating with the inner cylinder consisted of a copper wire about 1 mm. in diameter, and was connected to the wire I leading to the electrometer by means of an insulated brush of brass wires bearing partly on one side and partly on the other. This

arrangement was satisfactory, except that sudden large disturbances were rather frequent. An earlier arrangement consisting of a steel needle running in a drop of mercury seemed rather better; the substitution was made in trying to locate a very troublesome disturbance, which was finally traced to a minute looseness of the needle. The electrometer was placed on a separate pier about 6 feet from the apparatus and in line with it, the connecting wire lying approximately along the axis. The sensitiveness was raised by means of a concave lens from 3000 to about 18,000 mm./volt at 4 m. distance; the spot could be read when stationary to 0.2 mm. Electrometer and connecting wire were carefully screened and the windings of the solenoid were connected to earth through 10,000 ohms in order to render definite any residual electrostatic effects.

No means being at hand to record the instantaneous speed of rotation, a device was adopted which gave a reading proportional to the product of field-strength and speed. A Faraday disk A was mounted on the end of the shaft, and a galvanometer giving about 3×10^{10} mm./amp. was connected through a megohm to a brush of four brass wires bearing on the bottom of the groove in the disk, and to a second brush sliding opposite the earthing brush on the knob B.

§ 3. *Method of Observation.*

Since setting the condenser in rotation caused a deflexion of several centimetres, readings were taken only by varying the magnetic field at steady speed. Let Q_1 be the charge held on the inner cylinder of the condenser by electromagnetic induction, and let Q =total charge on inner cylinder, connecting wire, and electrometer, C =capacity of this system, and V =potential of electrometer and connecting wire. Then

$$Q = Q_1 + CV.$$

If, now, the magnetic field is altered, Q_1 is altered; and if the system is insulated a deflexion of the electrometer will result corresponding to a change in its potential of

$$V = -\frac{1}{C} \Delta Q_1.$$

The usual method was to set the apparatus in rotation and insulate the electrometer; then read the spot and throw on

the current; after 20 seconds, read again and reverse the current; after another 20 seconds, read again and throw off the current; after another 20 seconds, take a final reading. This gives, by subtraction, three deflexions. The electrometer was not quite dead-beat, but reached the end of its swing in just 20 seconds; intervals of this length were marked out by a torsion-pendulum actuating a sounder. The galvanometer also was not quite dead-beat, but reached the end of its swing in 15 seconds, so its extreme position was read in each instance, giving three galvanometer deflexions likewise. Sets of readings were taken in groups of four so as to eliminate all effects that did not change sign both with the current and with the direction of rotation.

The apparent deflexion due to throwing the magnetic field on was calculated by adding twice the middle deflexion, reversed in sign, to the other two and dividing the sum by 6; drift is thus eliminated. The result is a little too large because of the underdamping; but the necessity for making a correction was avoided by taking comparison readings in exact imitation of the principal ones, using a known source of potential.

A current of 25 amp. was usually employed, and full speed was about 2000 R.P.M.

§ 4. *Calculation of Charge on Inner Cylinder.*

It is easily shown that any point of the apparatus metallically connected to earth comes to a potential of Np elmg. units, where p =rev. per sec. and N =flux encircled by the point in each revolution. Accordingly, the magnetic flux through various sections of each cylinder and the shaft was compared with that through the central section of the outer cylinder by means of a ballistic galvanometer; a null method was employed and great care was taken to eliminate stray effects. It was found that the flux through any section was proportional to the area of the section and to the sum of the angles subtended by the mean ends (radius 4.93 cm.) of the solenoid, with a maximum correction of 2 per cent., and this fact was utilized in calculating additional values.

The calculation now reduces to the solution of the following electrostatic problem: given the potentials over the bounding surfaces of two spaces each having the form of a right cylindrical shell, to find the distribution of electrification. The work was done in steps so as to avoid the solution of

more than two simultaneous equations at a time. The result for the outer space was

$$V = V_0 \{ -\cdot 259 + 1\cdot 067 \log r \\ - \cosh (\cdot 327x) [\cdot 0205 J_0(\cdot 327r) + \cdot 0352 K_0(\cdot 327r)] \\ - \cosh (\cdot 292x) [\cdot 0027 J_0(\cdot 292r) - \cdot 0111 K_0(\cdot 292r)] \},$$

where x = distance along axis from centre, V_0 = potential at centre of outer cylinder, and

$$K_0 = J_0 \log x + \frac{x^2}{2^2}(1) - \frac{x^4}{2^2 4^2}(1 + \frac{1}{2}) \dots;$$

with a similar result for the inner space (between shaft and cylinder and guard-rings).

The charge on the insulated inner cylinder is the difference between the electric fluxes just outside and just inside the cylinder; this turns out to be $(-7\cdot 62 + 1\cdot 40)V_0 = -6\cdot 22V_0$. From the degree of accuracy of the work and the following analysis of possible sources of error, it appears that the solution result should be accurate to one-half per cent.

The residual error in the boundary values of the potential exceeded $0\cdot 003V_0$ only over the end plates and near the end of the outer cylinder, where it rose quickly to $0\cdot 04V_0$. The effect of the rather large error over the end plates may be estimated by assimilating the space to a rectangular slab and employing as an approximate harmonic the expression

$$Ae^{-\frac{\pi z}{r_2-r_1}} \sin \pi \frac{r-r_1}{r^2-r_1^2}. \quad \text{It is easily shown that even if } A \text{ were}$$

equal to V the effect of such a term upon the insulated cylinder would be negligible. Evidently the same must be true of the small error near the end of the outer cylinder. The connecting wire will also be charged, but the charge on the part of it inside the shaft is easily shown to be negligible by treating it as one coating of a small condenser. The longitudinal part attached to the cylinder will be at a lower potential than would exist at that point in the absence of the wire, because the potential due to induction is proportional to r^2 , while that due to the charges will contain chiefly $\log r$; hence the wire will be negatively charged. Calculation shows that the difference in potentials would be about $0\cdot 03V_0$; estimating the capacity of the wire at $2/3$ elst. unit, we have a charge on it of $-0\cdot 02V_0$.

Turning now to the amber insulators,—if the entire space were filled with amber there would be no effect upon the distribution of electrification*; but here we have to do with

* E. H. Kennard, *Phys. Zeits.* Dec. 1, 1912, p. 1155; March 15, 1913, p. 256.

short rings, and they were also flattened on opposite sides to a depth of some 3 mm. Now a rather long calculation by the method of the first article cited shows that an amber shell extending the whole length of the space and from the shaft to within 3 mm. of the inner cylinder would increase the electric flux by something like 40 per cent. In the actual case the amber extended only an eighth of the length of the insulated cylinder, and was flattened over less than half of the circumference, so that the effect could hardly exceed 2 per cent. of the flux; and this would result in an extra charge of only $0.02 \times 0.140V_0 = 0.03V_0$. This correction just about cancels the one due to the connecting wire.

§ 5. *Determination of the Theoretical Effect.*

A rough estimate of the deflexions to be expected can now be made as follows. A current of 25 amp. would produce an induction of 1600 gaussses inside the solenoid, and a flux through the central section of the inner surface of the outer cylinder of about 55,400. At a speed of 33 rev. per sec. this gives a difference of $V_0 = 0.0183$ volt between outer cylinder and axis; the charge on the inner cylinder will therefore be $6.22 \times 0.0183 \times 1/300 = 0.114 \times 1/300$ elst. unit. The total capacity was found to be 138 elst. units; hence with a sensitiveness of 18,000 mm./volt the establishment of the magnetic field will cause a deflexion of $0.117 \times 18,000 \div 138 = 14.9$ mm. If in fig. 1 the direction of the magnetic field is from left to right and the top of the condenser is moving out of the paper, then the outer cylinder will be at a higher potential than the axis, and the inner cylinder will be negatively charged; establishment of the field will cause a deflexion of the electrometer in the direction of positive potential.

For an accurate test of theory the ratio between electrometer and galvanometer deflexions was employed. For the comparison readings a potential of $V = 0.02$ volt (about) was applied to the electrometer case, which was used as a standard inductor, and simultaneously exactly one-tenth of this was applied through the megohm to the galvanometer; by applying, reversing, and removing the potential, readings were taken in imitation of the principal ones. The electrometer readings agreed within 2 per cent., and averaged 20.5 mm., while the galvanometer deflexion was 62.2 mm. The coefficient of influence of the electrometer case had been compared previously by a null method with a good guarding condenser, whose capacity was computed to be 40.1 elst. units, and was found to be 7.42. On the other hand, the

flux through the Faraday disk was found with a ballistic galvanometer to be 0·1197 of that through the central section of the outer cylinder, so that in the main experiment the E.M.F. in the galvanometer circuit was 0·1197V₀. Hence, by proportion, the ratio of the deflexions due to induction should be

$$\frac{20\cdot5}{62\cdot2} \cdot \frac{\cdot 1V}{\cdot 1197V_0} \cdot \frac{6\cdot22V_0}{7\cdot42V} = 0\cdot231.$$

§ 6. *The Electromagnetic Induction Effect.*

The final results on the rotation of the solenoid alone and of solenoid and condenser locked together are shown in the annexed table. Columns S and I give the direction of rotation and the initial direction of current respectively, E and G are the electrometer and galvanometer deflexions, and R is their ratio. "Rev. av." denotes the average effect reversing with current and direction of rotation. Four sets of readings were rejected for very obvious good reason, and at once replaced; and perhaps as many more sets were not completed because of the occurrence of an obvious large disturbance. To illustrate the character of the separate readings: the three electrometer deflexions for the first line in the table were +8·5, +4·8, +3·7; for the second, +22·4, +13·8, +1·8; for the fifth, +5·1, -39·1, +3·3; for the sixth, -12·6, +29·9, -21·5.

| | S. | I. | E. | G. | R. |
|---------|----|----------|---------|---------|------|
| Sol.... | — | + | + 4 mm. | + 5 mm. | |
| | — | — | + 6 | — 3 | |
| | + | — | — 1·1 | — 6 | |
| | + | + | + 3·5 | + 2 | |
| | | | <hr/> | <hr/> | |
| | | Rev. av. | + 1·2 | 0 | |
| Both... | + | + | +14·4 | +60·7 | ·237 |
| | — | + | —15·6 | —65·7 | ·237 |
| | — | — | +16·4 | +69·4 | ·236 |
| | + | — | —18·0 | —69·8 | ·258 |
| | | | | <hr/> | |
| | | | | Av. | ·242 |

Final Observations.

The first group of results confirms Barnett's conclusion that the electromagnetic effect of rotating the solenoid alone is *nil*. A similar group taken previously ranged from ·8 to 2·7 mm., and gave a reversing effect of only +2 mm.

For the case where solenoid and condenser are set in rotation at the same speed and in the same direction, the mean value of the ratio 0.242 is 5 per cent. larger than the theoretical value of 0.231. But immediately after these observations a similar group of four sets taken at half speed gave a mean ratio of 0.228 (range .211 to .263), which is 1.4 per cent. too small. Then a group was taken at full speed but by a different method: in quick succession the observer threw on the current, insulated the electrometer, read the spot, and reversed the current; after 20 seconds another reading was taken and the current was turned off, and after another 20 seconds a final reading was taken. This gives two deflexions in opposite directions, a third of whose numerical sum should be the electromagnetic effect. The values thus obtained ranged from .195 to .271, and averaged 0.238; including three readings rejected because the first reading was not the greater, the average becomes 0.241. Proportionality of the effect to current strength had been tested previously; a group of four sets using 13 amp. gave a mean ratio (not comparable with the previous values) of .25, while a group taken under the same conditions, but using 25 amp., gave .27.

With the condenser alone rotating final observations were not obtained because the solenoid became short-circuited, and it was not thought worth while to rewind it. The case is, however, deducible from the other two by simple superposition; and partial confirmation is furnished by a group of observations which were taken under about the same conditions, and gave a mean electrometer deflexion of 14 mm.

The results thus remain somewhat rough, but they seem sufficient to warrant the conclusion with fair certainty that the condenser becomes charged by its own rotation in the manner required by Lorentz's theory, independently of the rotation of the solenoid.

§ 7. *Fate of the Moving-Line Theory.*

The view has been put forward by Poincaré*, Abraham†, and Barnett‡ that even observations on open circuits cannot disprove the moving-line theory; and in reply to criticism by the author, Barnett maintained this view with some heat§.

* H. Poincaré, *Écl. Élect.* xxiii. p. 41 (1900).

† Abraham & Föppl, *Theo. der Elektr.* p. 420.

‡ S. J. Barnett, *Phys. Rev.* Nov. 1912, p. 323.

§ S. J. Barnett, *Phys. Rev.* Oct. 1913, p. 323.

The author yields to none in appreciation of Barnett's work on unipolar induction, and in respect for his long experience with electromagnetic theory; but on this point it seems clear that all of the writers mentioned have, through an oversight, arrived at a wrong conclusion.

The matter has been fully discussed elsewhere*, but perhaps a summary of the argument will not be amiss here. Barnett urges that an adherent of the moving-line theory must suppose the lines (*i. e.* the rotating magnetic system) to set up *in the æther* the same electromotive intensity that is caused to act upon a material dielectric, and shows from this assumption that the charges developed upon conductors would be the same whether the lines moved or not. The objection which seems to the author conclusive is that this electromotive intensity, of magnitude $\frac{1}{c}[\mathbf{V} \times \mathbf{B}]$, does not in general satisfy Laplace's equation. (The proof is simple.) In spite of this fact Barnett employs the two additional assumptions:

$$f = \frac{1}{c}[\mathbf{V} \times \mathbf{B}] + e + \mathbf{E}, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where f = total electromotive intensity, e = electric force due to changes in the magnetic field and vanishes in the present instance, \mathbf{E} = electric force due to electrostatic causes alone; and the equation

$$\text{div}(\mathbf{K}f) = 4\pi\rho, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where ρ = electric density.

Now in free æther we know from electrostatics that $\text{div} \mathbf{E} = 0$. Hence in free æther $\text{div} f = \frac{1}{c} \text{div}[\mathbf{V} \times \mathbf{B}]$, and may not vanish, which contradicts (2). We are thus forced to the conclusion that if the moving-line theory is correct, then the lines do not act on the æther, but only on material bodies, and instead of (2) we must write (with Lorentz) $\text{div}(\mathbf{K}\mathbf{E}) = 4\pi\rho$.

The real root of the matter seems to be that the æther cannot be treated as only a particular species of the genus "dielectric," but must be regarded as complementary to all material dielectrics. The displacement or polarization in matter does not need to be solenoidal, because its sources can be cancelled by sources of opposite sign in the displacement in the æther, and the total displacement may then be

* E. H. Kennard, *Phys. Rev.* May 1913, p. 355.

solenoidal. But free æther has no such means of self-defence, and consequently all forces acting on it must themselves be solenoidal.

The moving-line theory seems therefore to be definitely disposed of by the results obtained by Barnett, Fehrle, and the author.

§ 8. Conclusion.

The practical bearing of these experiments is small, yet they do necessitate a correction of certain statements that are common in the textbooks. For instance, it is not correct to say that the effect of rotating the armature of a dynamo is the same as that of rotating the field-magnets in the opposite direction. The *total* E.M.F. is the same, but in the first case it is developed almost entirely in the longitudinal parts of the winding, while in the second case a large fraction of it is developed in the radial parts, and the distribution of electrification on the armature will be different.

The most interesting case theoretically is that where the solenoid and condenser rotate together at the same speed. The charging up of the condenser cannot be conditioned by rotation relative to the connecting wires and electrometer. For suppose that the sliding contacts had been exactly on the axis, which was nearly true, and that they were connected by an axial wire extending through the condenser so as to form a closed circuit. Then it is certain, by Faraday's law, that rotation of the connecting wires and electrometer would cause no deflexion of the latter; and this negative result can hardly be due to an E.M.F. in the axial wire which was added. Rotation relative to the earth might in some unknown way be responsible for the observed effect, but this seems improbable. If we reject this assumption, then the effect is due to an absolute rotation in the same sense in which the operation of a gyrocompass is due to an absolute rotation of the earth.

But rotation of the whole is essentially only translation of the parts. We must suppose each electron in the condenser to experience a radial force proportional to its distance from the axis; and it is interesting to inquire what can cause such a force. It cannot be due either to the radial acceleration, for that is proportional to the square of the distance, nor to a possible rotation of the electron about its axis, for that should be the same for all electrons, nor to their motion relative to other essential parts of the apparatus, for there is no such motion. Apparently the only remaining alternative is to ascribe the force to motion of the electrons relative to

something which is not matter, and which does not share in the rotation of the condenser, and this something must be the stationary æther of Lorentz.

This phenomenon seems therefore to lend definite support to the existence of an electromagnetic æther. It is, perhaps, the only low-frequency phenomenon which cannot easily be described in terms of "action at a distance" between electrons and atoms. It seems, for this reason, to have some importance as a stumbling-block in the way of those ultra-relativitists who would abandon the conception of an æther altogether.

Summary.

An experiment is described showing that a cylindrical condenser rotating inside a magnetized coaxial solenoid becomes charged as required by the theory of Lorentz. Rotation of the solenoid has no effect (Barnett).

The disproof of the moving-line theory is thus completed ; electromagnetic induction depends in part upon absolute rotation in the mechanical sense. Analysis in terms of electrons seems to make necessary the existence of a stationary æther in order to explain the observed effect ; so that the phenomenon seems to present difficulties for those relativitists who reject the æther.

It is a pleasure to acknowledge obligations to Mr. Christian Dane, mechanician, whose share in the construction of the apparatus left nothing to be desired ; and to Professor Henry A. Erikson for his kindly interest and advice during the progress of the work.

University of Minnesota,
August, 1916.

XIV. *The Limits of Inflammability of Gaseous Mixtures.* By W. M. THORNTON, D.Sc., D.Eng., Professor of Electrical Engineering in Armstrong College, Newcastle-upon-Tyne*.

1. **T**HE ignition of an inflammable gas mixed with air depends in a variety of ways upon the proportion of oxygen present. With impulsive sparks or condenser-discharge the ignition passes through critical stages when the ratios of the number of oxygen atoms to one molecule of

* Communicated by the Author.

gas are whole numbers*. It will be shown that the proportions of oxygen in the limiting mixtures are in regular systems.

Burgess and Wheeler have shown† that in the case of the paraffins the lower limit of inflammability is inversely proportional to the calorific value of the gas, but this is also the case when the number of oxygen atoms in the limit mixture bears the same proportion in each gas to those required for perfect combustion. It seemed therefore worth while to examine whether in general the proportion of oxygen in the limiting mixtures has any definite relation to that for perfect combustion.

The following are values of the limits recently observed: n is the number of oxygen atoms required for the normal combustion of one molecule m of the gas. A mixture $m+n$ gives this condition.

TABLE I.

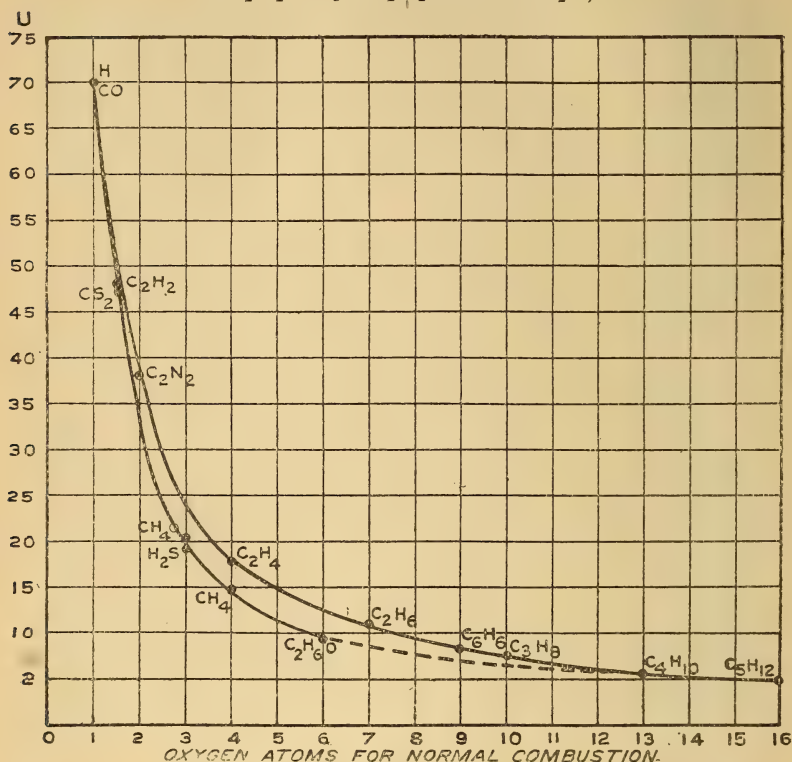
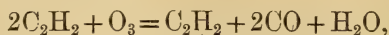
| Gas. | Upper Limit. $U_{\text{obs.}}$ | n . | nU . | Nearest whole number composition. | $U_{\text{cal.}}$ |
|----------------------|-----------------------------------|-------|--------|---|-------------------|
| Hydrogen | 60 | 1 | 60 | $4m+n$ | 62.2 |
| Methane..... | 14.8 | 4 | 59.2 | $2m+n+1$ | 14.1 |
| Ethane | 10.7 | 7 | 74.9 | $2m+n$ | 10.5 |
| Propane..... | 7.35 | 10 | 73.5 | $2m+n$ | 7.6 |
| Butane | 5.7 | 13 | 74.1 | $2m+n$ | 5.9 |
| Pentane | 4.5 | 16 | 72.0 | $2m+n$ | 4.9 |
| Methyl alcohol | 21.0 | 3 | 63.0 | $2m+n$ | 21.6 |
| Ethyl alcohol | 9.5 | 6 | 57.0 | $3m+2n$ | 9.35 |
| Hydrogen sulphide. | 19.0 | 3 | 57.0 | $2m+n$ | 21.6 |
| Carbon monoxide ... | 70.0 | 1 | 70.0 | $6m+n$ | 71.2 |
| Benzene | 8.0 | 9 | 72.0 | $2m+n$ | 8.4 |
| Acetylene | 46.0 | 3/2 | 69 | $3m+n$ | 45.0 |
| Ethylene | 17.5 | 4 | 70 | $2m+n$ | 17.1 |
| Cyanogen | 38.0 | 2 | 76 | $3m+n$ | 38.2 |
| Carbon disulphide.. | 45.0 | 3/2 | 67.5 | $3m+n$ | 45.0 |

The products nU are fairly constant in one of two groups, as shown in the figure. On the upper curve, that of the heavier paraffins, the product is between 69 and 75; in the lower, that of methane, between 57 and 65.

* "The Ignition of Gases by Condenser Discharge Sparks," Proc. Roy. Soc. A. vol. xci. p. 17 (1914). "The Ignition of Gases by Impulsive Electrical Discharge," Proc. Roy. Soc. A. vol. xcii. p. 381 (1916).

† "The Lower Limit of Inflammation of Mixtures of the Paraffin Hydrocarbons and Air," by M. J. Burgess and R. V. Wheeler, Chem. Soc. Journ. vol. xcix. p. 2013 (1911).

The normal ignition of benzene* is to CO. This is also true for cyanogen† and probably for ethylene‡. The critical mixture for acetylene§ is



the mixture for complete combustion being passed through without any change of inflammability. The same would appear to be the case for carbon disulphide, and in both of these the ratio of oxygen to combustible gas burnt to CO is 3/2.

2. The empirical equations in column 5 represent the nearest whole number mixtures to give the observed upper limit. The values calculated from these are given in the last column. As an example of the use of the empirical

* "The Electrical Ignition of Gaseous Mixtures," Proc. Roy. Soc. A. vol. xc. p. 281 (1914).

† "Ignition by Impulsive Discharge," *l. c.* p. 396.

‡ "Ignition by Impulsive Discharge," *l. c.* p. 393.

§ "Ignition by Impulsive Discharge," *l. c.* p. 394.

formula, ethane may be chosen. In this case the upper limit is at $2\text{C}_2\text{H}_6 + \text{O}_7$, giving $\frac{4 \times 100}{4 + 7 \times 4.85} = 10.53$ per cent. of gas in air. The agreement between the calculated and observed values shows that in the upper limit mixtures of the paraffins *there is twice the volume of inflammable gas as in the mixture for perfect combustion*. In certain endothermic compounds, acetylene, cyanogen, and carbon disulphide, there is three times this volume, in hydrogen four, and in carbon monoxide six times. The upper limits of inflammability of any gas in a homologous series of which the first terms are known can then be calculated from the equation typical of the compound.

3. While the upper limit mixtures of the paraffins contain twice as much combustible gas as those for perfect combustion, ignition fails at the lower limit when there is twice as much oxygen, being first possible when there is one atom of oxygen less than this. The mixture $m + 2n$ is uninflammable, $m + (2n - 1)$ is the lower limit for the paraffins. In the case of ethane it is at $\text{C}_2\text{H}_6 + \text{O}_{13}$, which gives a percentage of $\frac{2 \times 100}{2 + 13 \times 4.85} = 3.08$ in air.

TABLE II.

| Gas. | n . | $L_{\text{obs.}}$ | Nearest mixture $m + nL$. | $L_{\text{cal.}}$ | LmL . |
|----------------------|-------|-------------------|-------------------------------|-------------------|---------|
| Hydrogen | 1 | 4.1 | $m + 9n$ | 4.4 | 36.9 |
| Methane | 4 | 5.6 | $m + (2n - 1)$ | 5.5 | 39.2 |
| Ethane | 7 | 3.1 | $m + (2n - 1)$ | 3.08 | 40.2 |
| Propane | 10 | 2.17 | $m + (2n - 1)$ | 2.12 | 41.2 |
| Butane..... | 13 | 1.55 | $m + (2n - 1)$ | 1.62 | 38.8 |
| Pentane | 16 | 1.35 | $m + (2n - 1)$ | 1.31 | 41.8 |
| Benzene | 15 | 1.5 | $m + (2n - 1)$ | 1.4 | 43.5 |
| Methyl alcohol | 3 | 5.5 | $m + (3n - 2)$ | 5.5 | 38.5 |
| Ethyl alcohol..... | 6 | 2.8 | $m + (3n - 2)$ | 2.5 | 44.8 |
| Acetylene | 5 | 3.0 | $m + (3n - 2)$ | 3.0 | 39.0 |
| Cyanogen | 4 | 7.6 | $m + (3n - 2)$ | 7.6 | 76.0 |
| Carbon disulphide .. | 6 | 2.5 | $m + (3n - 2)$ | 2.5 | 40.0 |
| Hydrogen sulphide. . | 3 | 4.5 | $m + 3n$ | 4.47 | 40.5 |
| Carbon monoxide ... | 1 | 12.6 | $m + 3n$ | 12.1 | 37.8 |
| Ethylene..... | 6 | 5.7 | $m + (n + 1)$ | 5.57 | 39.9 |
| Mean..... | | | | | 40.1 |

The paraffins form one group in which benzene falls, as it did at the upper limit, acetylene, cyanogen, and carbon disulphide, with the alcohols, another. Cyanogen falls into

line with the others if its combustion in the explosion wave, even in dilute mixtures, is to CO and not to CO₂. In this case n is 2 and $Ln_L=38$. It has been shown previously that the upper limit is inversely proportional to the number n of oxygen atoms burnt. At the lower limit oxygen is in excess, but it is now found that the product Ln_L of the percentage of gas and of the number of oxygen atoms in the lower limit mixtures, given in the last column of Table II., is also constant. Since both Un and Ln_L are fixed their ratio is constant. But in all homologous series of gases n/n_L is sensibly constant. It follows that the *ratio of the upper to the lower limits of inflammability should be nearly constant*. In the paraffins this ratio increases slightly, in the ethylene series it decreases, as shown in Tables III. and IV.

4. Since the product of the percentage L of combustible gas in the lower limit mixture and of the oxygen atoms present per molecule of combustible gas is constant, *the number of oxygen atoms is the same in unit volume of the lower limit mixtures of all inflammable gases*. These atoms are not all burnt, but as they are all raised to the temperature of ignition it follows that they are all activated, and that *the intensity of pioneering ionization or activation of oxygen in the advancing wave-front is the same in all gases at the point where self-ignition begins*.

The percentage U is a measure of the number of combustible molecules in unit volume of the upper limit mixture; and since the heat of combustion of each molecule of a hydrocarbon can be shown to be approximately proportional to n , the product Un is proportional to the *total heat of combustion of unit volume, and this is the same in the upper limit mixtures of all groups of gases in which Un has the same value*.

Both the upper and lower limits of inflammability can then be considered as controlled by the heat liberated in the reaction, and this would bring the facts stated into line with current views. It is not, however, the heat set free that controls the oxygen that can be present and so decides the percentage of gas, but the oxygen that controls the heat, so that behind the thermal effects there are the conditions of Tables I. and II. Inflammation can only occur when certain numerical relations exist between the oxygen and gas molecules.

5. It is possible from the above to predict the limits of inflammability of certain groups of compounds with fair hope of accuracy. The heavier paraffins as far as octane

form the chief constituents of petrol*; refined lamp oils are composed of still heavier paraffins with a few olefines†. In Table III. the limits have been calculated from the formulæ derived from the lighter paraffins. U and L are percentages of combustible gas in air: their ratio is nearly constant and may be compared with the experimental values.

TABLE III.

| Compound. | | <i>n</i> . | $\frac{U_{\text{cal.}}}{2m+n}$ | $\frac{L_{\text{cal.}}}{m+(2n-1)}$ | $\left(\frac{U}{L}\right)_{\text{cal.}}$ | $\left(\frac{U}{L}\right)_{\text{obs.}}$ |
|-------------------|---------------------------------|------------|--------------------------------|------------------------------------|--|--|
| Methane | CH ₄ | 4 | 14.1 | 5.5 | 2.56 | 2.74 |
| Ethane..... | C ₂ H ₆ | 7 | 10.5 | 3.08 | 3.41 | 3.45 |
| Propane | C ₃ H ₈ | 10 | 7.6 | 2.12 | 3.58 | 3.39 |
| Butane..... | C ₄ H ₁₀ | 13 | 5.9 | 1.62 | 3.64 | 3.66 |
| Pentane | C ₅ H ₁₂ | 16 | 4.9 | 1.31 | 3.74 | 3.60 |
| Hexane | C ₆ H ₁₄ | 19 | 4.16 | 1.10 | 3.77 | |
| Heptane | C ₇ H ₁₆ | 22 | 3.61 | 0.95 | 3.80 | |
| Octane..... | C ₈ H ₁₈ | 25 | 3.19 | 0.84 | 3.80 | |
| Nonane | C ₉ H ₂₀ | 28 | 2.86 | 0.74 | 3.84 | |
| Decane | C ₁₀ H ₂₂ | 31 | 2.59 | 0.67 | 3.86 | |
| Endecane | C ₁₁ H ₂₄ | 34 | 2.37 | 0.61 | 3.87 | |
| Dodecane | C ₁₂ H ₂₆ | 37 | 2.18 | 0.56 | 3.88 | |
| Tridecane | C ₁₃ H ₂₈ | 40 | 2.02 | 0.52 | 3.89 | |
| Tetradecane | C ₁₄ H ₃₀ | 43 | 1.88 | 0.48 | 3.91 | |
| Pentadecane | C ₁₅ H ₃₂ | 46 | 1.77 | 0.45 | 3.91 | |
| Mean..... | | | | | 3.84 | |

Olefines are present in petroleum; their limits of inflammability, based on ethylene, the only gas observed experimentally, are given in Table IV.

TABLE IV.

| Compound. | | n_{CO_2} | n_{CO} | $\frac{U}{2m+n_{\text{CO}}}$ | $\frac{L}{m+(n+1)_{\text{CO}_2}}$ | $\frac{U}{L}$ |
|-----------------|---------------------------------|-------------------|-----------------|------------------------------|-----------------------------------|---------------|
| Ethylene | C ₂ H ₄ | 6 | 4 | 17.09 | 5.57 | 3.07 |
| Propylene | C ₃ H ₆ | 9 | 6 | 12.07 | 3.96 | 3.05 |
| Butylene | C ₄ H ₈ | 12 | 8 | 9.35 | 3.08 | 3.04 |
| Amylene | C ₅ H ₁₀ | 15 | 10 | 7.63 | 2.51 | 3.04 |
| Hexylene..... | C ₆ H ₁₂ | 18 | 12 | 6.43 | 2.12 | 3.03 |
| Heptylene | C ₇ H ₁₄ | 21 | 14 | 5.56 | 1.84 | 3.03 |
| Octylene | C ₈ H ₁₆ | 24 | 16 | 4.91 | 1.62 | 3.03 |
| Diamylene | C ₁₀ H ₂₀ | 30 | 20 | 3.96 | 1.31 | 3.03 |
| Triamylene..... | C ₁₅ H ₃₀ | 45 | 30 | 2.67 | 0.88 | 3.03 |
| Tetramylene ... | C ₂₀ H ₄₀ | 60 | 40 | 2.02 | 0.67 | 3.01 |

* "The Gas, Petrol and Oil Engine," D. Clerk, F.R.S., and G. Burls, vol. ii. p. 448.

† *Loc. cit. supra*, p. 440.

The observed limits for ethylene are 17.5 and 5.7, their ratio being 3.07. The other compounds agree well enough with this to support the calculated limits.

These values are given for the purpose of furnishing a guide for the experimental examination of the limits of inflammability, and as showing how any constituent hydrocarbon in petrol or "paraffin" mixtures with air is likely to affect their range of ignition.

XV. *The Relation of Oxygen to the Heat of Combustion of Organic Compounds.* By W. M. THORNTON, D.Sc., D.Eng., Armstrong College, Newcastle-upon-Tyne*.

1. **T**HE heats of combustion of the hydrocarbons (C, H) can be expressed by the formula

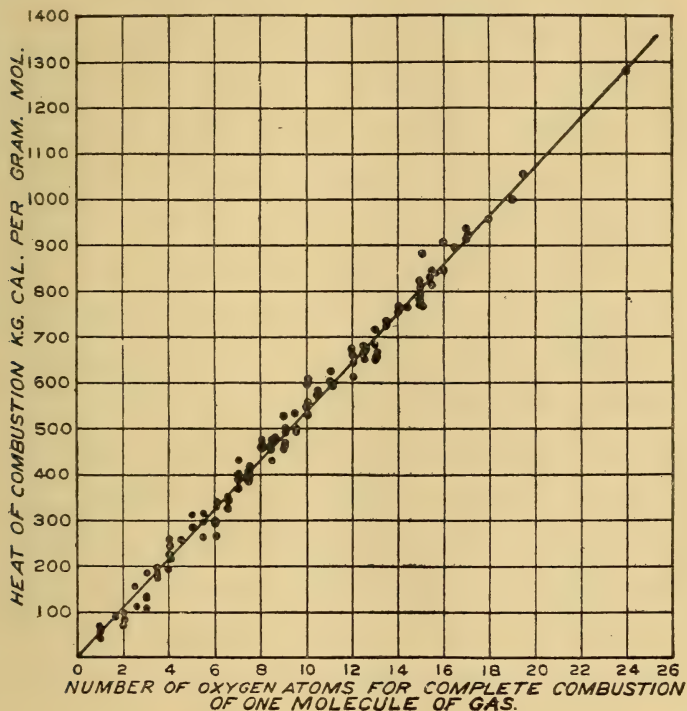
$$(C_a, H_{2b}) = aA + bB - \Sigma v,$$

in which A and B are the heats of combustion of carbon and hydrogen respectively to CO_2 and H_2O , Σv being the internal energy represented by the bonds. For the paraffins and related compounds $A = 105.92$ large calories per gram molecule, $B = 52.42$; for the aromatic hydrocarbons $A' = 107.16$, $B' = 51.78$. In both cases the heat of combustion of carbon is very nearly twice that of hydrogen. This numerical relation, which may only be accidental, leads to a singularly convenient law for the estimation of the calorific value of any hydrocarbon of known composition. Thus the difference between the heats of combustion of successive members of the paraffins, olefines, acetylenes, aromatic hydrocarbons, alcohols, aldehydes, ketones, and esters is also nearly constant and is equal to 158.57 calories, for the radicle CH_2 . $A + B$ in the above formula = 158.34, $A' + B' = 158.94$, the mean being 158.59. Since these effects are additive, when combustion is complete with one oxygen atom the heat set free, irrespective of bonds, is 52.4 calories per gram molecule of combustible gas, when with two atoms 105.9, with three 158.59.

2. Taking the heats of combustion H of hydrocarbons and other compounds, without attempting to discuss their energy of internal strain, and dividing them by the number of oxygen atoms necessary for complete combustion, values of H/n are obtained, which under the conditions are remarkably constant. These are given in the Tables below, in which the compounds of Tables 35 to 44 in Thomsen's 'Thermochemistry' are taken for examples. It is difficult from such

* Communicated by the Author.

a series of values to estimate relative differences; for this purpose the figure has been drawn, having for ordinates the measured heats of combustion, and for abscissæ the oxygen atoms required in each case.



Many of the points overlap; there are in all 121. A straight line drawn from the farthest point to zero passes through them so closely that 55 touch it. The heat of combustion is therefore as a first approximation proportional to the number of oxygen atoms which combine with a molecule of combustible gas, irrespective of molecular complexity and of whether it is carbon or hydrogen that is burnt, and is found to be equal to $53n$ large calories per gram molecule. This can scarcely be accidental; it has the appearance of representing a general action. What it suggests as the essential feature of combustion is that oxygen is first sensitized by contact with the source of ignition and becomes an immensely active agent, atoms of which are able to seize upon and tear apart the almost unresisting hydrocarbon molecule. The heat of the reaction, being all translational

energy, is the result of the speed with which the oxygen atoms rush into combination, and is therefore proportional only to their number. There is much in the general phenomena of ignition to support this view, especially in the sudden changes of inflammability which occur when the ratios of the oxygen atoms to those of combustible gas are whole numbers. It is, however, capable of interpretation in many instances in terms of the regular occurrence of the CH_2 radicle, as suggested by my colleague Dr. J. A. Smyth, and the most satisfactory agreements are found in such cases. On the other hand, it suggests that the heat of combustion of carbon being twice that of hydrogen may not be altogether accidental, but may be an example of this general relation from which the value for CH_2 is itself derived.

3. An interesting departure from this is found in the nitro-compounds. The complete combustion of nitro-methane CH_3NO_2 requires only $1\frac{1}{2}$ atoms of oxygen numerically, if the oxygen in the molecule is used in its combustion. Its heat of combustion is 180·9, and H/n is here 120·5. So great a ratio is not found in any of the previous compounds.

The oxygen required to burn the carbon and hydrogen is $3\frac{1}{2}$ atoms, and if this is taken instead of $1\frac{1}{2}$, $\text{H}/n=51\cdot7$ bringing it into line. This can only mean that the oxygen contained in these compounds takes no part in their combustion, owing perhaps to the difficulty of activating it when associated with nitrogen, and that in these cases combustion is all carried out by free oxygen. This opens a question as to the part played by combined oxygen in explosives.

TABLE I.

| Compound. | Molecular formula. | Oxygen atoms n for complete combustion. | Molecular heat of combustion. H. | $\frac{\text{H}}{n}$. |
|------------------------|---------------------------|---|----------------------------------|------------------------|
| Paraffins. | | | | |
| Methane | CH_4 | 4 | 211·9 | 53·0 |
| Ethane..... | C_2H_6 | 7 | 370·4 | 53·0 |
| Propane | C_3H_8 | 10 | 529·2 | 52·9 |
| Butane..... | C_4H_{10} | 13 | 687·2 | 52·9 |
| Pentane | C_5H_{12} | 16 | 847·1 | 53·0 |
| Hexane | C_6H_{14} | 19 | 999·2 | 52·2 |
| Aromatic Hydrocarbons. | | | | |
| Benzene | C_6H_6 | 15 | 799·3 | 53·1 |
| Toluene | C_7H_8 | 18 | 955·7 | 53·1 |
| Mesitylene | C_9H_{12} | 24 | 1282·3 | 53·5 |
| Pseudocumene | C_9H_{12} | 24 | 1281·5 | 53·5 |

| Compound. | Molecular formula. | Oxygen atoms <i>n</i> for complete combustion. | Molecular heat of combustion. H. | $\frac{H}{n}$. |
|-----------|--------------------|--|----------------------------------|-----------------|
|-----------|--------------------|--|----------------------------------|-----------------|

Unsaturated Hydrocarbons.

| | | | | |
|-------------------------|-------------|-----|-------|------|
| Ethylene | C_2H_4 | 6 | 333·3 | 55·5 |
| Propylene, normal | C_3H_5 | 8·5 | 429·7 | 58·0 |
| Trimethylene | C_3H_6 | 9 | 499·4 | 55·5 |
| Isobutylene | C_4H_{10} | 13 | 650·6 | 50·5 |
| Isoamylene | C_5H_{10} | 15 | 807·6 | 53·8 |
| Diallyl | C_6H_{10} | 17 | 932·8 | 54·9 |
| Acetylene | C_2H_2 | 5 | 310·0 | 62·0 |
| Allylene | C_3H_4 | 8 | 467·5 | 58·4 |
| Dipropargyl | C_6H_6 | 15 | 882·8 | 58·9 |

Halogen Compounds.

| | | | | |
|------------------------------|--------------|------|-------|------|
| Methyl chloride | CH_3Cl | 3·5 | 176·9 | 50·6 |
| Ethyl chloride | C_2H_5Cl | 6·5 | 344·1 | 53·0 |
| Propyl chloride | C_3H_7Cl | 9·5 | 492·3 | 51·8 |
| Isobutyl chloride | C_4H_9Cl | 12·5 | 650·1 | 52·0 |
| Monochlorethylene | C_2H_3Cl | 5·5 | 298·3 | 54·3 |
| Monochlorpropylene | C_3H_5Cl | 8·5 | 453·3 | 53·4 |
| Allyl chloride | C_3H_5Cl | 8·5 | 454·7 | 53·5 |
| Phenyl chloride | C_6H_5Cl | 14·5 | 763·8 | 52·7 |
| Ethylene chloride | $C_2H_4Cl_2$ | 6 | 296·3 | 49·4 |
| Ethylidene chloride | $C_2H_4Cl_2$ | 6 | 296·4 | 49·4 |
| Chloracetol | $C_3H_6Cl_2$ | 9 | 453·8 | 50·5 |
| Carbonyl chloride | $COCl_2$ | 1 | 41·8 | 41·8 |
| Chloroform | $CHCl_3$ | 2·5 | 107·0 | 42·8 |
| Monochlorethylene chloride.. | $C_2H_3Cl_3$ | 5·5 | 262·5 | 47·7 |
| Tetrachlormethane | CCl_4 | 2 | 75·9 | 37·9 |
| Tetrachlorethylene..... | C_2Cl_4 | 4 | 195·0 | 48·8 |
| Methyl bromide | CH_3Br | 3·5 | 184·7 | 52·8 |
| Ethyl bromide | C_2H_5Br | 6·5 | 341·8 | 52·6 |
| Propyl bromide | C_3H_7Br | 9·5 | 499·3 | 52·6 |
| Allyl bromide | C_3H_5Br | 8·5 | 462·1 | 54·4 |
| Methyl iodide | CH_3I | 3·5 | 196·0 | 56·0 |
| Ethyl iodide | C_2H_5I | 6·5 | 353·7 | 54·4 |

Ethers and Acetals.

| | | | | |
|-----------------------------|----------------|----|-------|------|
| Ethylene oxide | C_2H_4O | 5 | 312·5 | 62·5 |
| Dimethyl ether | C_2H_6O | 6 | 349·3 | 58·2 |
| Methylethyl ether | C_3H_8O | 9 | 505·8 | 56·2 |
| Diethyl ether | $C_4H_{10}O$ | 12 | 659·6 | 54·9 |
| Methylallyl ether | C_4H_8O | 11 | 627·2 | 57·0 |
| Diallyl ether | $C_6H_{10}O$ | 16 | 911·1 | 56·9 |
| Methylpropargyl ether | C_4H_6O | 10 | 603·8 | 60·3 |
| Anisol | C_7H_8O | 17 | 936·3 | 55·1 |
| Methylal | $C_3H_8O_2$ | 8 | 476·1 | 59·5 |
| Methal orthoformate | $C_4H_{10}O_3$ | 10 | 599·1 | 59·9 |

| Compound. | Molecular formula. | Oxygen atoms n for complete combustion. | Molecular heat of combustion. H. | $\frac{H}{n}$. |
|-------------------------------|-------------------------------------|---|----------------------------------|-----------------|
| Alcohols. | | | | |
| Methyl alcohol | CH_4O | 3 | 182.2 | 60.7 |
| Ethyl alcohol | $\text{C}_2\text{H}_6\text{O}$ | 6 | 340.5 | 56.8 |
| Propyl alcohol | $\text{C}_3\text{H}_8\text{O}$ | 9 | 498.6 | 55.4 |
| Isopropyl alcohol | $\text{C}_3\text{H}_8\text{O}$ | 9 | 493.3 | 54.8 |
| Isobutyl alcohol | $\text{C}_4\text{H}_{10}\text{O}$ | 12 | 658.5 | 54.8 |
| Trimethyl carbinol | $\text{C}_4\text{H}_{10}\text{O}$ | 12 | 641.3 | 53.5 |
| Isoamyl alcohol..... | $\text{C}_5\text{H}_{12}\text{O}$ | 15 | 820.0 | 54.7 |
| Dimethyl ethyl carbinol | $\text{C}_6\text{H}_{12}\text{O}$ | 17 | 810.4 | 47.7 |
| Allyl alcohol | $\text{C}_3\text{H}_6\text{O}$ | 8 | 464.7 | 58.1 |
| Propargyl alcohol | $\text{C}_3\text{H}_4\text{O}$ | 7 | 431.1 | 61.6 |
| Phenyl alcohol | $\text{C}_6\text{H}_6\text{O}$ | 14 | 768.7 | 54.9 |
| Ethylene glycol | $\text{C}_2\text{H}_6\text{O}$ | 6 | 298.1 | 49.7 |
| Aldehydes and Ketones. | | | | |
| Acetic aldehyde | $\text{C}_2\text{H}_4\text{O}$ | 5 | 281.9 | 56.4 |
| Propionic aldehyde | $\text{C}_3\text{H}_6\text{O}$ | 8 | 440.7 | 55.1 |
| Isobutyric aldehyde | $\text{C}_4\text{H}_8\text{O}$ | 11 | 599.9 | 54.5 |
| Dimethyl ketone..... | $\text{C}_3\text{H}_6\text{O}$ | 8 | 437.2 | 54.6 |
| Methyl propyl ketone | $\text{C}_5\text{H}_{10}\text{O}$ | 14 | 754.2 | 53.9 |
| Acids and Acid Anhydrides. | | | | |
| Formic acid | CH_2O_2 | 1 | 69.4 | 69.4 |
| Acetic acid | $\text{C}_2\text{H}_4\text{O}_2$ | 4 | 225.3 | 56.4 |
| Propionic acid | $\text{C}_3\text{H}_6\text{O}_2$ | 7 | 386.5 | 55.2 |
| Acetic anhydride | $\text{C}_4\text{H}_6\text{O}_3$ | 8 | 460.0 | 57.5 |
| Esters. | | | | |
| Methyl formate | $\text{C}_2\text{H}_4\text{O}_2$ | 4 | 241.2 | 60.3 |
| Methyl acetate | $\text{C}_3\text{H}_6\text{O}_2$ | 7 | 399.3 | 57.1 |
| Ethyl formate | $\text{C}_3\text{H}_6\text{O}_2$ | 7 | 400.0 | 57.1 |
| Methyl propionate..... | $\text{C}_4\text{H}_8\text{O}_2$ | 10 | 553.9 | 55.4 |
| Ethyl acetate | $\text{C}_4\text{H}_8\text{O}_2$ | 10 | 546.5 | 54.6 |
| Propyl formate | $\text{C}_4\text{H}_8\text{O}_2$ | 10 | 558.8 | 55.8 |
| Methyl isobutyrate | $\text{C}_5\text{H}_{10}\text{O}_2$ | 13 | 716.9 | 55.2 |
| Isobutyl formate | $\text{C}_5\text{H}_{10}\text{O}_2$ | 13 | 719.9 | 55.4 |
| Allyl formate..... | $\text{C}_4\text{H}_6\text{O}_2$ | 9 | 527.9 | 58.7 |
| Dimethyl carbonate | $\text{C}_3\text{H}_6\text{O}_3$ | 6 | 357.5 | 59.6 |
| Diethyl carbonate | $\text{C}_5\text{H}_{10}\text{O}_3$ | 12 | 674.1 | 56.2 |
| Ethyl nitrate | $\text{C}_2\text{H}_5(\text{NO}_3)$ | 6.5 | 324.0 | 49.9 |
| | $\text{C}_2\text{H}_5(\text{NO}_3)$ | 3.5 | 324.0 | 92.6 |

| Compound. | Molecular formula. | Oxygen atoms n for complete combustion. | Molecular heat of combustion. H. | $\frac{H}{n}$. |
|---|--------------------|---|----------------------------------|-----------------|
| Mercaptans, Sulphides, Sulphocyanides, &c. | | | | |
| Hydrogen sulphide | H_2S | 3 | 136·7 | 45·6 |
| Methyl hydrosulphide | CH_4S | 6 | 298·8 | 50·0 |
| Ethyl hydrosulphide..... | C_2H_6S | 9 | 455·6 | 50·6 |
| Dimethyl sulphide..... | C_2H_6S | 9 | 457·3 | 50·8 |
| Diethyl sulphide | $C_4H_{10}S$ | 15 | 772·1 | 51·5 |
| Thiophene | C_4H_4S | 12 | 610·6 | 50·9 |
| Methyl sulphocyanide | C_2H_5SN | 7·5 | 398·9 | 53·3 |
| Methyl isosulphocyanide | C_2H_5NS | 7·5 | 392·0 | 52·3 |
| Allyl mustard oil | C_4H_5NS | 12·5 | 675·3 | 54·0 |
| Carbon disulphide..... | CS_2 | 6 | 265·1 | 44·2 |
| Carbonyl sulphide..... | COS | 3 | 131·0 | 43·7 |

Cyanogen, Hydrogen Cyanide, Nitrates, and Amines.

| | | | | |
|------------------------|--------------|------|--------|------|
| Cyanogen | C_2N_2 | 4 | 259·6 | 64·9 |
| Hydrogen cyanide | HCN | 2·5 | 158·6 | 63·5 |
| Acetonitrile | C_2H_3N | 5·5 | 312·1 | 56·7 |
| Propionitrile | C_3H_5N | 8·5 | 471·4 | 55·4 |
| Ammonia | H_3N | 1·5 | 90·6 | 60·4 |
| Methylamine | CH_5N | 4·5 | 258·3 | 57·5 |
| Dimethylamine | C_2H_7N | 7·5 | 420·4 | 56·1 |
| Trimethylamine..... | C_3H_9N | 10·5 | 582·6 | 55·5 |
| Ethylamine | C_2H_7N | 7·5 | 415·6 | 55·4 |
| Diethylamine | $C_4H_{11}N$ | 13·5 | 734·5 | 54·4 |
| Triethylamine | $C_6H_{15}N$ | 19·5 | 1052·3 | 54·0 |
| Propylamine | C_3H_9N | 10·5 | 575·7 | 54·8 |
| Isobutylamine | $C_4H_{11}N$ | 13·5 | 725·3 | 53·7 |
| Amylamine..... | $C_5H_{13}N$ | 16·5 | 890·5 | 54·0 |
| Allylamine | C_3H_7N | 9·5 | 531·2 | 54·9 |
| Aniline..... | C_6H_7N | 15·5 | 838·4 | 54·1 |
| Pyridine | C_5H_5N | 12·5 | 675·0 | 54·0 |
| Piperidine | $C_5H_{11}N$ | 15·5 | 833·8 | 54·1 |

Nitro-compounds, Nitrites, and Nitrates.

| | | 1. | 2. | | 1. | 2. |
|------------------------|-----------------|------|------|-------|------|-------|
| Nitromethane..... | CH_3NO_2 | 3·5 | 1·5 | 180·9 | 51·7 | 120·5 |
| Nitroethane | $C_2H_5NO_2$ | 6·5 | 4·5 | 337·9 | 52·0 | 75·1 |
| Ethyl nitrite | $C_2H_5NO_2$ | 6·5 | 4·5 | 334·2 | 51·4 | 74·3 |
| Isobutyl nitrite | $C_4H_9NO_2$ | 12·5 | 10·5 | 647·6 | 51·8 | 61·7 |
| Amyl nitrite | $C_5H_{11}NO_2$ | 15·5 | 13·5 | 812·6 | 52·4 | 60·2 |
| Ethyl nitrate | $C_2H_5NO_3$ | 6·5 | 3·5 | 324·0 | 49·9 | 92·4 |

5. From the relation $H = 53n$ the quantity of air required for the complete combustion of any hydrocarbon of unknown composition, such as a petrol substitute, can be found when

the heat of combustion and the vapour density d are known. The heat of combustion is sometimes given in British Thermal Units per pound. The molecular weight of a gas is $28.87d$, and since there are 252 small calories in one B.T.U. and 454 grams to the pound,

$$n = \text{B.T.U. per lb.} \times 252 \times 28.87 \times d / 53 \times 454 \times 10^3.$$

$$= 3.025 \times \text{B.T.U.} \times d \times 10^{-4}.$$

Taking, for example, the petrol mixtures examined by Thomas and Watson, quoted by Clerk and Burls*, we obtain the values of n in Table II., and the percentage mixtures in air giving this, the ratios of the volumes of air and vapour, and of their weights. Since the substance consists mostly of paraffins n will be in general a whole number. In order to bring Thomas and Watson's heats of combination into line with those for the paraffins, which have been closely determined, they have been multiplied by 1.13.

TABLE II.

| Compound. | Calorific value. B.T.U. per lb. | Vapour density at 0° C. 760 mm. Air=1. | $n_{\text{cal.}}$ from formula. | n known. | Per cent. of gas in air for perfect combustion. | Vols. of air to one of inflammable vapour. | Weight of air weight of vapour. |
|------------------|---------------------------------|--|---------------------------------|------------|---|--|---------------------------------|
| Methane | 23,800 | 0.554 | 3.98 | 4 | 9.35 | 9.7 | 17.5 |
| Ethane | 21,500 | 1.074 | 7 | 7 | 5.5 | 17.2 | 16.0 |
| Butane | 21,300 | 2.01 | 12.95 | 13 | 3.07 | 31.5 | 15.6 |
| Pentane | 21,200 | 2.51 | 16.06 | 16 | 2.51 | 38.8 | 15.45 |
| Hexane..... | 21,200 | 2.99 | 19.15 | 19 | 2.13 | 46.0 | 15.4 |
| Heptane | 21,150 | 3.45 | 22.1 | 22 | 1.84 | 53.3 | 15.45 |
| taken | | | | | | | |
| Bowley's | 21,600 | 3.05 | 20 | 20 | 2.02 | 48.5 | 15.9 |
| Carless | 21,200 | 3.11 | 20 | 20 | 2.02 | 48.5 | 15.6 |
| Express..... | 20,400 | 3.35 | 21.2 | 21 | 1.92 | 51.2 | 15.26 |
| Ross | 21,100 | 3.33 | 21.4 | 21 | 1.92 | 51.2 | 15.35 |
| Pratt (a) | 21,030 | 3.16 | 20.2 | 20 | 2.02 | 48.5 | 15.35 |
| Pratt (b) | 20,090 | 3.20 | 20.6 | 21 | 1.92 | 51.2 | 16.0 |
| Carburine | 21,120 | 3.28 | 21.9 | 22 | 1.84 | 53.3 | 16.28 |
| Shell ordinary. | 21,150 | 3.27 | 21.9 | 22 | 1.84 | 53.3 | 16.32 |
| Dynol | 20,930 | 3.43 | 21.7 | 22 | 1.84 | 53.3 | 16.55 |
| Simcar benzol. | 19,300 | 3.24 | 18.9 | 19 | 2.13 | 46 | 14.2 |
| 0.760 (Baillie). | 20,950 | 3.29 | 21.4 | 21 | 1.92 | 51.2 | 15.6 |
| 0.760 Shell ... | 20,620 | 3.36 | 21.8 | 22 | 1.84 | 53.3 | 15.9 |
| Coaline..... | 18,850 | 3.31 | 18.9 | 19 | 2.13 | 46 | 13.9 |
| Mean values... | 20,700 | 3.26 | 20.7 | 20.7 | 1.95 | 50.4 | 15.5 |

* 'The Gas, Petrol, and Oil Engine,' vol. ii. p. 452.

The values of n for the paraffins calculated from the formula, using observed calorific values and vapour densities, are very close to the known numbers, and those found for the fuel mixtures can probably be accepted to the same degree of certainty. It is noticeable that the ratio of the weight of air for complete combustion to that of the vapour burnt is highest in methane and falls rapidly to a normal value in butane. The mean ratio for all the substances is 15.5 lb. of air to one of fuel, and the variations are small. The mean number of oxygen atoms for complete combustion of the mixtures is 20.7, corresponding to a mixture of almost equal proportions of hexane and heptane if these alone are present.

6. In the same way when the calorific value of any liquid or gaseous fuel is unknown, it can be determined by finding by explosion the volume of air required to burn completely a measured volume of the vapour of known density. If, for example, 50 volumes of air are required for one of vapour, and the measured vapour density is 3.2, the percentage of gas is 1.96, $n=20.4$, and the heat of combustion
$$= \frac{20.4 \times 10^4}{3.025 \times d} = 21,100 \text{ B.T.U. per lb. of fuel, or } H=1100$$
 large calories per gram molecule.

XVI. On Discontinuous Wave-Motion : Part II.

By C. V. RAMAN, M.A., and ASHUTOSH DEY*.

[Plate III.]

IN an important paper on the theory of discontinuous wave-propagation†, Harnack has given an elegant general formula expressing the mode of vibration of a string whose configuration is completely determined by a finite number of discontinuous changes of velocity travelling over it. As an illustration of his result, Harnack has discussed, in some detail, the cases in which the form of vibration is determined by one and by two such changes of velocity respectively. The analysis indicates that the case of a single discontinuity is identical with that of the principal mode of vibration of a bowed string, and in a previous communication from this laboratory‡ it has been shown

* Communicated by the Authors.

† A. Harnack, *Mathematische Annalen*, vol. xxix. p. 486.

‡ C. V. Raman, M.A., and S. Appaswamaiyar, "On Discontinuous Wave-Motion." *Phil. Mag.* Jan. 1916.

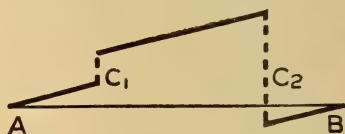
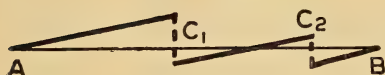
how this mathematical result may be confirmed experimentally. The general case of two discontinuities considered by Harnack covers a considerable and interesting variety of forms of vibration, and the method described in the previous paper has now been successfully extended so as to obtain an experimental confirmation of Harnack's results in some of these cases also.

Experimental Method.

If C_1 and C_2 represent two discontinuous changes of velocity travelling on a string of finite length which completely determine its motion, the velocity-diagram of the string must in general consist of three parallel straight lines as shown in fig. 1 (a) or fig. 1 (b). Each of the two outer

Fig. 1 (a).

Fig. 1 (b).



lines passes through one of the fixed ends of the string and is separated from the intermediate line by a discontinuity.

In fig. 1 (a) the discontinuities are of the same sign, and in fig. 1 (b) they are of opposite signs. A velocity-distribution similar to that shown in either of the figures would be obtained if a string has initially a uniform angular velocity about a point in its own line, and if in the course of this motion the two points A and B are suddenly fixed, either simultaneously or else successively, at an interval less than that necessary for an impulse to travel from A to B or *vice versa*. If the point about which the string has initially a uniform angular velocity lies within AB, we have the case shown in fig. 1 (a). If it lies in BA produced, the velocity-distribution is similar to that shown in fig. 1 (b). The photographic records presented with this paper (Pl. III. fig. 2) refer to a case in which the string has initially a uniform angular velocity about a point lying outside the two fixed stops A and B, and the discontinuous changes of velocity which determine the form of vibration are therefore of opposite signs.

The method by which the records are obtained is similar to that described in the previous paper, but with certain necessary modifications. The tension and initial motion of the string are, as before, secured by a weight attached to its

free end, which is allowed to swing down in the manner of a pendulum. The stops A and B are placed approximately in a vertical line below the point of suspension of the string. As soon as the string impinges on the lower stop B, the weight swings inwards, and the end B is thus effectually fixed. The upper stop A, however, presents some difficulty as it is practically in the same line as that joining B with the point of suspension, and does not therefore, except at the first impact, effectually fix the string at A. To avoid this difficulty, a small cylinder of soft iron is fixed to the string midway between A and its point of suspension, and an electromagnet is provided which, when the string reaches the vertical position carrying the cylinder with it, draws the latter inwards and then holds it. The stop at A is thus rendered completely effective. The initial motion at any point on the string between A and B and its subsequent vibration are photographically recorded on sensitive paper contained in a dark-slide, which moves downwards behind an illuminated slit set across the string*.

When the position of the stops A and B is such that the string impinges upon both simultaneously, the impulses cross one another midway between A and B, and the resultant vibration is then necessarily symmetrical. The first six records shown in the Plate refer to the motion at different points when this condition is practically attained. The last record, however, shows a different case, in which the string is fixed at the stop A an appreciable interval after it is fixed at B. This condition is attained by drawing A a little out of the straight line joining B and the point of suspension. The discontinuities cross elsewhere than at the centre of the string twice in each period of vibration, and the vibration-curves are then necessarily asymmetrical. This is evident from the record shown.

Theory.

The theoretical form of the vibration-curve at any specified point may be deduced from the velocity-diagram. For, the velocity at any given point on the string is unaffected by the motion of the discontinuities except when one of them actually passes over it. The successive velocities and the

* For facility of work, it is arranged that the weight and string are released electromagnetically. Simultaneously an auxiliary pendulum is released, which after an adjustable interval of time breaks a contact and releases the photographic slide.

intervals for which they subsist are thus known, and the vibration-curve which represents the resulting displacements may be plotted from these values without difficulty. The records shown in the Plate are found to be completely in agreement with the results thus obtained. The special feature of interest is that the vibration-curves are seen to be intermediate in form between the two-step zigzags of a bowed string and those characteristic of a plucked string*. The reason for this is not far to seek. When one of the discontinuities is zero, we have, as already seen, the case of the bowed string. When $C_1 = -C_2$, the motion reduces exactly to that of a string plucked at the point at which the discontinuities cross. The cases actually recorded in these experiments are those in which C_1 and C_2 are unequal but of opposite signs, and are thus intermediate between the two extreme types referred to above.

The cases in which C_1 and C_2 are of the same sign are also of interest in connexion with the theory of the special forms of vibration of a bowed string obtained at the "wolf-note" pitch, and also under other conditions when the vibration-curves assume the form of four-step zigzags. Experiments are being undertaken to reproduce these special forms of vibration by the method indicated in this paper.

Summary and Conclusion.

In these experiments, the characteristic vibration-forms produced by the motion of two unequal discontinuous changes of velocity of opposite sign have been observed and recorded photographically. Some are of the symmetrical type and the others are asymmetrical. The results are in full agreement with the mathematical theory first given by Harnack. The vibration-curves are found to be intermediate in form between those characteristic of bowed and of plucked strings. The cases in which the discontinuities are of the same sign are also of special acoustical interest and will be studied separately.

The Indian Association for the
Cultivation of Science, Calcutta,
29th September, 1916.

* Krigar-Menzel and Raps, *Sitzungsberichte* of the Berlin Academy, 1893, p. 509.

Note added on the 23rd of December.

1. The experimental work for the cases in which C_1 and C_2 are of the same sign and of various magnitudes, has since been completed and will be described in the third paper of this series shortly to be published. The results obtained have an important application in the theory of the *Cyclical forms* of vibration of a bowed string which may be obtained under a very wide variety of conditions, of which the phenomenon noticed at the "wolf-note" pitch forms only one example (Phil. Mag. October 1916, p. 395).

2. In the paper on the "wolf-note" just cited, in parag. (c) on page 395, for the word "A-string" read "D-string." Further work has shown that the possibility of a "cyclical" vibration depends not so much on the length of the string as on its frequency. On the D-string of the 'cello I use, cyclical vibrations may be obtained by suitable bowing over a very wide range of frequencies, from 160 to 180 vibrations per second, from 230 to 370 vibrations per second, and even at higher frequencies. Though cyclical forms are usually obtained only when the bow is applied near one end of the string, they may also be noticed under favourable conditions when the bow is applied not far from some important node, *e. g.*, near the point of bisection or trisection of the string. It has also been noticed that in certain cases a periodic (not cyclical) vibration may be maintained, the frequency of which is *not* independent of the speed, pressure, or place of bowing.

XVII. *An Atomic Model.* By R. R. RAMSEY, Ph.D., Associate Professor of Physics, Indiana University, Bloomington, Ind., U.S.A.*

MODERN theories of the structure of an atom assume one or more electrons in motion about a central body or positive nucleus. Probably the experiment which has been the most helpful in giving an idea as to the structure of an atom is the Mayer† experiment of the floating needles. This, together with the work of J. J. Thomson‡, has become almost classic.

The experiment gives an idea of the possible structure of atoms, and may account for the periodic variations of the properties of the atoms. Thus one, by assuming that an atom of large atomic weight has more electrons than one of

* Communicated by the Author.

† 'Scientific American,' Supplement, vol. v. p. 2045, June 22, 1878.

‡ 'The Corpuscular Theory of Matter,' p. 107.

small atomic weight, may account for the periodic table, as has been done by Lyon. (Phys. Rev. vol. iii. p. 232, 1914.)

The classical method of performing the experiment is by floating magnetized needles by means of corks in water. I have found that small bicycle-balls floated on mercury are much more convenient. (Professor Merritt used this method at Cornell University in 1900.) The mercury surface lends itself admirably for projection with reflected light. In projection it is well to focus not on the balls, but on a plane a short distance above the balls, or on the focal point of the concave mirror made by the depression caused by the balls. The position of the ball is then shown on the screen as a point of light.

In the classical Mayer experiment the balls are fixed. There is nothing to suggest how the atom may radiate. The atom is dead. The motion of the atom must be imagined. It is usual to imagine the needles to rotate about the centre with a constant angular velocity. This is contrary to the laws of planetary motion as illustrated in the solar system.

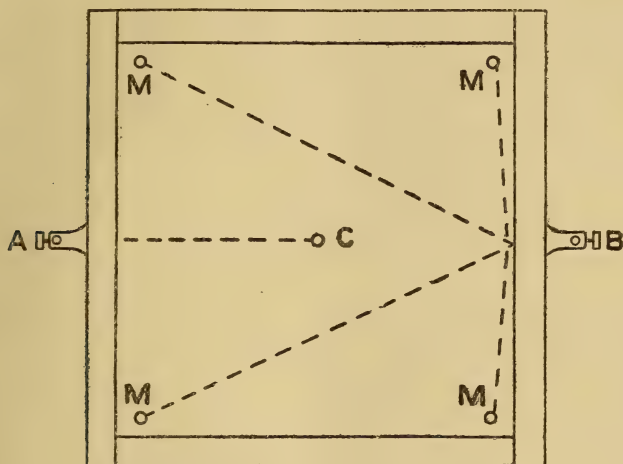
While working with this experiment the thought came to me to rotate the mercury, and thus to rotate the balls. A wooden tray was made with an electrode at the centre and four electrodes, one at each corner, which were connected in multiple. By sending the current in at the middle electrode and out at the corners one has an approximately radial current flowing at right angles to the magnetic field of the magnet, which plays the part of the positive nucleus in the experiment. This causes the mercury to rotate and carry the balls with it.

The apparatus consists of a wooden tray, as shown in fig. 1. The dimensions are 15×15 cm. and 2 cm. in depth. The electrodes C and M are made of platinum. (It has been found later that the electrodes M can be made of iron without appreciably distorting the magnetic field.) A and B are binding posts which are connected to the electrodes by wires, shown by dotted lines, which are in grooves on the under side of the box. The apparatus can be centred up by placing one bicycle-ball on the mercury surface after the current has been turned on through both the magnet and the tray, and then shifting the tray until the ball remains practically stationary at the centre of the rotating mercury.

When two balls are placed on the rotating surface they do not rotate about the centre on the same circle, as one would expect from the Mayer experiment. No. 1 first rotates about No. 2, and then No. 2 rotates about No. 1. Their paths resembling rotating ellipses. With three balls the motion is

more complicated, the three balls taking turns in the centre. The motion reminds one of a complicated game of leap-frog. With a number of balls the motion becomes very complicated.

Fig. 1.



The mercury at the edges of the box is stationary while the central portion is rotating. The angular velocity increases as we go from the edge to the centre. The balls floating on the surface tend to take up the same angular velocity as the mercury upon which they float. There is a tendency for the balls to take up a motion which may approximate to planetary motion. Thus we may assume that they obey Kepler's law.

In the Mayer experiment, when the balls are stationary, when there are a number of rings any one ball is held in its place by the central force of the magnet and the mutual repulsion of the neighbouring balls. The balls of one ring fit into the crotches of the neighbouring rings. When the balls are not stationary and the angular velocity of the outer ring is less than that of the inner ring, there is a slipping of one ring with respect to the one next to it. This slipping produces a perturbation or a vibratory motion which is superimposed on the regular circular motion. This perturbation may be said to be the source of some sort of radiation, light perhaps.

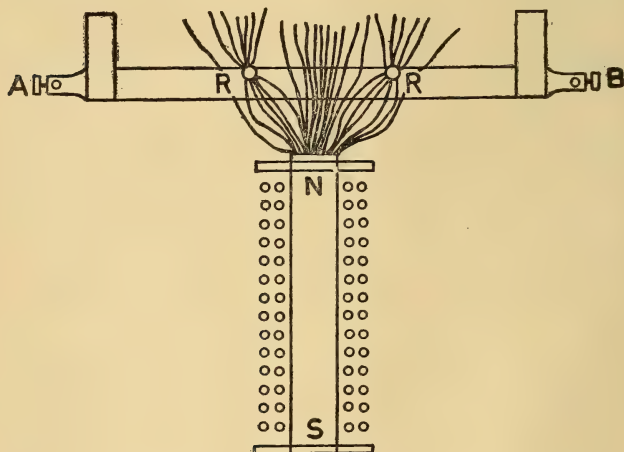
When a ball from the outside is allowed to come into the system there is a great disturbance of the whole system. If the balls represent electrons, this disturbance may be said to be the source of the X rays, as when a cathode ray hits a platinum atom, say.

With a large number of balls the motion is very much more complicated than one would expect. At times a ball will start out from the outer ring and apparently seem to try to escape from the system. In consequence of the friction of the mercury and the nature of the field, the ball always returns. If a ball were to escape it would cause a rearrangement of the others, or a disturbance similar to that caused by an added ball. This tendency of the ball to fly off is especially great if the current through the mercury is increased, or if the system absorbs energy. This may be an illustration of what takes place in the photo-electric effect, or in the case of ionization produced by hot bodies.

In the case when a ball flies out when rotating at normal or constant velocity, we have an explanation of γ rays caused by β rays. Or we may let the balls represent α rays, helium atoms, or that which in the atom of radium makes α rays or helium atoms after they have escaped, and we have an illustration of a radioactive substance.

To illustrate the disintegration of an atom of radium through its several disintegration products, I made a tray in which I embedded a ring of iron, so as to make a magnetic field which is strong at the centre and diminishes as we go along any radius, passing through a minimum and then

Fig. 2.



through a maximum over the ring of iron. Fig. 2 is a cross-section of the tray and central magnet. N S is the central magnet. R R is the cross-section of the iron ring. A and B are binding posts by which the current is led in

and out. The variation of the field is represented by lines of force.

To use this the current is turned on the magnet and a number of balls are placed in the centre of the tray, forming the characteristic figure due to the particular number as in the Mayer experiment. The current is then turned through the tray causing the balls to rotate. When a ball at irregular intervals starts out on a tangent, it will be caught and held by the intense field over the iron ring at R. Thus if the ball represents an α particle, the escape of β rays and the γ radiation may be explained as being due to the disturbance in the atom due to the rearrangement in the atom.

As many as eight or ten balls may escape from the system, each rearrangement of the system representing one of the products in the radioactive series.

Getting the conditions right is a matter of trial. Some three or four trays were made before one was satisfactory. The dimensions of this tray are as follows: length 10 cm., breadth 10 cm., depth 2 cm. The iron ring is made of a $2\frac{1}{2}$ millimetre rod bent into a ring of 6 cm. diameter.

No doubt many analogies will occur to the operator which have not been mentioned in this paper. The worst difficulty with the experiment is with the mercury. The mercury must be clean. Any film of dirt or dross on the surface of the mercury prevents the free motion of the balls.

The magnet and tray may be connected in series, but it is more convenient to have two circuits which may be manipulated independently.

Dept. of Physics,
Indiana University.
Nov. 7th, 1916.

XVIII. *On the Lubrication of Resistance-Box Plugs.* By J. J. MANLEY, *Daubeny Laboratory, Magdalen College, Oxford*.*

DURING March 1914, as a preliminary step in some work with platinum thermometers, it was necessary to standardize some resistance-coils. It soon became evident that for highly accurate work a distinct advantage would be gained if the plug-resistances of our several sets of coils could be made practically invariable. At the outset we tried to secure this object by frequently re-polishing the plugs and

* Communicated by the Author.

their seats with emery-dust paper ; and as a further aid to constancy each plug was used only for that seat in which it was found when the coils arrived from the makers.

When a plug is seated by the usual screw-like movement, the engaging surfaces tend to plough each other, and as a result burrs and grooves appear upon both. When a burr has been formed, its presence is easily detected by the characteristic gritty feeling which accompanies any displacement of the plug : the existence of a groove is readily verified with the aid of a lens. These burrs and grooves, which change in size, number, and form as the coils are used, appear to be entirely responsible for the variations observable in plug-resistance.

Now a too frequent re-polishing of the plugs, besides being highly inconvenient, is prejudicial to accuracy : we were therefore led to try the effect of several lubricants, and the plan was immediately successful.

In reply to an inquiry, Dr. Glazebrook, however, informs me that this method is not new, and that Mr. Price some 12 or 14 years ago showed that contact resistance is reduced by the application of petroleum either in the form of a film or bath, and that for some years past it has been the custom at the National Physical Laboratory to lubricate box-plugs and switches with paraffin ; and although no *special* description of the method has been published, allusions to the device have been made in various papers dealing with matters of a kindred nature. Under these circumstances it is believed that an account of some *quantitative* experiments recently carried out with the aid of five boxes of coils, may be helpful to other observers.

To begin with, the plugs and seats of box No. I. were polished and wiped with a clean cloth. Next, strips of stout writing-paper were, with the aid of resin cerate, fixed to the vertical faces of the row of brass blocks. As the upper edges of the paper were somewhat higher than the top of the blocks, a trough was thus formed, and this was filled with oil of the kind used in a Geryk pump. All the plugs having been normally seated, their joint resistance was measured by Carey Foster's method ; the plugs were then loosened, re-seated, and their resistance again determined : these several operations were performed 10 times, and from the 10 independent values a final mean value was calculated.

Secondly, the strips of paper were removed and the oil allowed to drain away, but the plugs and their seats were not wiped : a new series of measurements was then effected, and

from the results obtained another final mean value was calculated.

Thirdly, the oil was entirely removed, the plugs lubricated with medicinal paraffin oil, and a further series of observations proceeded with. For a fourth series the lubricant was "pure" vaseline.

Finally, the plugs, their seats and the ebonite top of the resistance-box were, with the aid of purified benzene, thoroughly freed from the lubricant, and a last series of determinations of the total plug-resistance carried out. The results of the several groups of measurements are set forth in Table A in the order in which they were obtained.

TABLE A.

Box No. I. Fitted with 9 plugs.

| Exper. | Resistance. | | | | |
|--------------|----------------------------------|------------------------------------|--|------------------------------|---------------------|
| | Plugs in bath of Geryk pump oil. | Plugs smeared with Geryk pump oil. | Plugs smeared with medicinal paraffin oil. | Plugs smeared with vaseline. | Plugs unlubricated. |
| | (1) | (2) | (3) | (4) | (5) |
| 1 | ·00170 | ·00112 | ·00094 | ·00109 | ·00101 ohm |
| 2 | 144 | 137 | 122 | 124 | 123 " |
| 3 | 116 | 137 | 131 | 109 | 188 " |
| 4 | 127 | 095 | 127 | 129 | 176 " |
| 5 | 131 | 117 | 142 | 109 | 194 " |
| 6 | 131 | 112 | 130 | 116 | 124 " |
| 7 | 131 | | | 124 | 127 " |
| 8 | 153 | | | 110 | 177 " |
| 9 | 122 | | | 124 | 166 " |
| 10 | 122 | | | 109 | 113 " |
| Means | ·00135 | ·00118 | ·00124 | ·00116 | ·00119 " |
| Max. value.. | ·00170 | ·00137 | ·00142 | ·00129 | ·00194 " |
| Min. " | ·00116 | ·00095 | ·00094 | ·00109 | ·00023 " |
| Variation = | ±·00027 | ±·00022 | ±·00024 | ±·00010 | ±·00086 |
| " = | ±20 per cent. | ±18·6 per cent. | ±19·3 per cent. | ±8·6 per cent. | ±72·2 per cent. |

Experiments were also tried with the plugs in a bath of medicinal paraffin; but as the results were practically identical with those given in the above series (3), it is not necessary to tabulate them here.

The data contained in Table A show that in every instance a distinct advantage is gained by lubricating the plugs. For two series, (1) and (3), the mean resistance of the oiled plugs is greater than the normal value (series (5)). In

accurate work this, however, is of no consequence as the plug-resistance must in any case be measured; but when this has been done, it is highly desirable that the resistance should remain invariable, and this end is, it appears, best attained by the use of vaseline. We now give in Table B summaries of the results obtained with three other second-class boxes.

TABLE B.

| | | Before lubricating. | After lubricating with vaseline. |
|------------------------------------|----------------------------|------------------------|-------------------------------------|
| Box No. II. having 17 plugs. | Number of determinations = | 10. | 10. |
| | Maximum total resistance = | ·00728 ohm. | ·00496 ohm. |
| | Minimum " " = | ·00452 " | ·00434 " |
| | Mean " " = | ·00593 " | ·00458 " |
| | Variation = | ±·00138 " | ±·00031 " |
| | Percentage " = | ± 23 | ± 6·1 |
| Box No. III. having 4 dials. | Number of determinations = | 7. | 7. |
| | Maximum total resistance = | 0·2357 ohm. | 0·0364 ohm. |
| | Minimum " " = | ·0385 " | ·0336 " |
| | Mean " " = | ·0990 " | ·0343 " |
| | Variation = | ±·0654 " | ±·0008 " |
| | Percentage " = | ± 66 | ± 2·3 |
| Box No. IV. having 17 plugs. | Number of determinations = | 10. | 10. |
| | Maximum total resistance = | ·01597 ohm | ·01241 ohm. |
| | Minimum " " = | ·01302 " | ·01148 " |
| | Mean " " = | ·01397 " | ·01188 " |
| | Variation = | ±·00079 " | ±·00031 " |
| | Percentage " = | ± 5·7 | ± 2·6 |

We observe that for each of the above-named boxes a very marked improvement was secured by the application of vaseline; and in the case of the dial-box (No. III.) the gain was very great. In general, we find that on bringing newly lubricated plugs or switches into use, their joint resistance diminishes for a short period, and then becomes for all practical purposes constant.

An oil-bath has this advantage over vaseline in that the plugs are automatically and fully lubricated with every setting; but, on the whole, vaseline is much more convenient in use, and in so far as we have been able to discover, the residual variations in plug-resistance are decidedly smaller than when a liquid lubricant is employed.

As confirmatory evidence of the beneficial effects attending the application of vaseline, we give in Table C a summary of the results obtained by experimenting with a first-class resistance-box fitted with 17 plugs.

TABLE C.

| | Before lubricating. | | After lubricating with vaseline. | |
|-----------------------------------|----------------------------|--|----------------------------------|-------------|
| | | | | |
| Box No. V. having 17 plugs. | Number of determinations = | | 9. | 9. |
| | Maximum total resistance = | | ·00248 ohm | ·00182 ohm. |
| | Minimum " " = | | ·00188 " | ·00162 " |
| | Mean " " = | | ·00217 " | ·00170 " |
| | Variation = | | ±·00016 " | ±·00007 " |
| | Percentage " " = | | ±7·4 | ±4·1 |

In this case the plugs had been fitted with great care: consequently we find that the variations in the resistance both before and after applying the lubricant are much smaller than in the cases previously cited.

XIX. *Dispersion and the Size of Molecules of Hydrogen, Oxygen, and Nitrogen.* By L. SILBERSTEIN, Ph.D., Lecturer at the University of Rome*.

THE molecular refractivity of an isotropic substance whose molecules consist of two equal atoms is given by

$$N = \frac{2}{3} N_0 \left[2 + \frac{1}{1 - \alpha N_0 / 2\pi R^3} \right],$$

where N_0 is the atomic refractivity,

$$\alpha = 3m_H / 1 \cdot 008 = 4 \cdot 88 \cdot 10^{-24} \text{ gr.},$$

and R the mutual distance of the "centres" of the two atoms composing each molecule, *i. e.* of the positions of equilibrium of the dispersive particles within their atoms †. We shall henceforth use the abbreviation

$$\sigma = \frac{\alpha}{2\pi R^3} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and write, therefore,

$$N = \frac{2}{3} N_0 \left[2 + \frac{1}{1 - \sigma N_0} \right] \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

It will be remembered that the dimensions of

$$N = \frac{\mu^2 - 1}{\mu^2 + 2} \frac{M}{d}$$

are $\text{cm.}^3 \text{ gr.}^{-1}$, so that σN_0 is a pure number. When the

* Communicated by the Author.

† Cf. Phil. Mag. vol. xxxiii. (1917), pp. 92–128. Throughout that paper, R^3 is to be replaced by $4\pi R^3$, our charges e , in formula (4) *et seq.*, being in rational units. Keeping this in mind, the above formula will be found identical with (24*b*) of the quoted paper. Another *erratum* is on p. 113, line 13, repeated in formula (30), where N_0 in the denominator should read $2N_0$; this, however, affects only the numbers of pp. 113–114 concerning a purely fictitious example. The subject will be taken up at a later opportunity in connexion with the real compounds C_2H_4 and C_2H_2 .

interatomic distance R is large enough for σN_0 to become a negligible fraction, then $N=2N_0$, as in the usual theory. The expression for N_0 itself is, in our previous symbols,

$$N_0 = \frac{B/\alpha}{\gamma_0 - \gamma} = \frac{B}{4\pi^2 c^2 \alpha} \cdot \frac{\lambda_0^2}{1 - (\lambda_0/\lambda)^2}, \quad . . . \quad (3)$$

where λ is the incident, and λ_0 the free wave-length belonging to each of the atoms, when undisturbed by its neighbours; $B=e^2/m$, m =mass, e charge of dispersive particle, in rational units.

In general, the atomic λ_0 will fall into the extreme ultra-violet, and since, in all cases to be treated hereafter, we shall limit ourselves to the visible region of the spectrum, the fourth and the higher powers of λ_0/λ will be negligible, so that

$$N_0 = b_0 + g_0/\lambda^2, \quad \quad (4)$$

where b_0 , g_0 , two constant attributes of the atom, are defined by

$$b_0 = \frac{B\lambda_0^2}{4\pi^2 c^2 \alpha}, \quad g_0 = b_0 \lambda_0^2, \quad \quad (5)$$

whence also

$$\frac{b_0^2}{g_0} = \frac{B}{4\pi^2 c^2 \alpha} = \frac{1.008}{12\pi^2 c^2} \left(\frac{e}{m}\right) \left(\frac{e}{m_H}\right), \quad . . \quad (6)$$

independent of the free wave-length. The latter formula will be useful in the sequel. Introducing (4) into (2), developing the denominator and rejecting the second and the higher powers of g_0/λ^2 , we have, for the molecular refractivity of the substance in question,

$$N = b + g/\lambda^2, \quad \quad (7)$$

where

$$\left. \begin{aligned} b &= \frac{2}{3} b_0 \left[2 + \frac{1}{1 - \sigma b_0} \right], \\ g &= \frac{2}{3} g_0 \left[2 + \frac{1}{(1 - \sigma b_0)^2} \right]. \end{aligned} \right\} \quad . . \quad (8)$$

Thus the *refraction-* and the *dispersion-coefficient* of the substance, as b , g may be called, appear as simple functions of the atomic coefficients b_0 , g_0 and of the interatomic distance involved in σ . Notice in passing that, the denominator $1 - \sigma b_0$ being a fraction (as in all concrete cases to be treated in the following sections), the dispersion will show a stronger departure from additivity than the refraction, which is a well-known feature of this class of phenomena. As to the range of σb_0 in connexion with the condition of stability, we shall return to it a little later on.

The simple problem to be treated in the present note, as an application of the general ideas laid down in the paper quoted above, will be this :

Given the molecular refractivity N of the diatomic substance, that is, given its coefficients b, g , find the atomic coefficients b_0, g_0 , and therefore the atomic refractivity N_0 , and also the interatomic distance R involved in σ .

These are three unknowns, while we have in (8) but two equations *. Thus far, therefore, the problem is indeterminate. In order to convert it into a determinate one, we shall have to make some assumption about the relation between b_0 and g_0 in each atom. For this purpose let us choose the obvious assumption that the value of b_0^2/g_0 belonging to each "dispersive particle" or atomic resonator is equal to an *exact multiple of the electronic value* of the right hand member of (6). More definitely, if ϵ be that electronic value, let us assume that, for any atom,

$$\frac{b_0^2}{g_0} = \kappa \epsilon, \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where κ is in each case *the smallest integer* compatible with the conditions of the problem. By "electron" we mean here the electron proper. Remembering that our charges e are in rational units, and taking for the specific charge

$\frac{1}{\sqrt{4\pi}} \frac{e/c}{m}$ that value, $1.77 \cdot 10^7$ c.g.s., which suits best the

observed typical cases of the Zeeman phenomenon and represents, at the same time, the mean of the more recent

* Theoretically one could say that b_0, g_0, σ are to be determined from three observed values of N , corresponding to three different wavelengths. But having once neglected higher powers of g_0/λ^2 and having therefore adopted the form (7), linear in λ^{-2} , we have *eo ipso* reduced any number of observations to two independent data only, b and g . The same would be the case if instead of the straight line (7), representing N as function of λ^{-2} we had taken a hyperbola analogous to (3). For this would again involve only two independent data. The rigorous curve of N is, by (25 b) *loc. cit.*, the superposition of two hyperbolæ, viz.

$$N = \frac{2B}{3\alpha} \left(\frac{2}{\gamma_0 - \gamma} + \frac{1}{\gamma' - \gamma} \right), \quad \gamma' = \gamma_0 - B/2\pi R^3,$$

so that, theoretically speaking, the three unknowns γ_0, B, R could be determined from three observed values of N . The actually available observations, however, are, notably in the case of the gases to be treated here, quite insufficient to distinguish the dispersion curve from a straight line. Thus, for the time being, we are driven by necessity to the linear form (7), amounting to two independent experimental data only, and the third datum must be supplied by some plausible assumption.

direct measurements by Classen, Wolz, and others*, we find

$$\epsilon = \frac{1.008}{3\pi} \frac{e/c}{m \sqrt{4\pi}} \frac{e/c}{m_H \sqrt{4\pi}} = 0.107 \cdot 1.77 \cdot 10^7 \cdot 9650 \\ = 183 \cdot 10^8 \frac{\text{cm.}}{\text{gr.}} \quad . \quad . \quad (10)$$

This is the numerical value to be substituted in (9). The assumption (9) can be put in words by saying that each atomic resonator consists of a certain number κ of electrons. In fact, provided that the distance of these electrons apart is large as compared with their radii†, the mutual mass will be negligible, so that their total mass will be κ times the mass, and their total charge κ times the charge of a single electron. Thus e/m will retain its value and e/m_H will be κ times greater. We need not enter into the mutual action of these κ electrons, but can treat them summarily by attributing to the whole system a single relevant free frequency $\sqrt{\gamma_0}$, which may already be the outcome of their co-operation together with the usual restitutive force.

But it seems safer to abstain from any such interpretation and to take our assumption as it is written down in (9). Merely for the sake of convenient language, this can be read as “atomic resonator consisting of κ electrons,” or “atom containing κ dispersive electrons.” The clause that κ should be the smallest integer compatible with the special conditions of the problem will be made clear presently.

Equations (8) with (9) are now sufficient for the determination of the two attributes b_0, g_0 of the atoms and of their mutual distance in the molecule. This will be done conveniently, in each of the concrete cases, in the following manner. To abbreviate, write

$$k = \frac{b^2}{g}, \text{ and } k_0 = \frac{b_0^2}{g_0} \quad . \quad . \quad . \quad (11)$$

Then k is known from experience, and $k_0 = \kappa\epsilon$. Dividing the square of the first by the second of (8), we have

$$k = 2k_0 \frac{3 - 4\sigma b_0 + \frac{4}{3}\sigma^2 b_0^2}{3 - 4\sigma b_0 + 2\sigma^2 b_0^2},$$

whence

$$\sigma b_0 = \frac{2k_0 - k \pm \sqrt{k(k_0 - \frac{1}{2}k)}}{\frac{4}{3}k_0 - k} \quad . \quad . \quad . \quad (12)$$

Now, k is essentially positive; thus the smallest value of

* Cf. Zeeman's ‘Researches in Magneto-optics’ (1913), p. 68 and *passim*.

† *I. e.* large compared with 10^{-13} cm., which, however, may still be a very small distance in comparison with atomic dimensions, 10^{-8} cm.

κ making σb_0 real will be the smallest integer κ satisfying the inequality

$$k_0 = \kappa \epsilon > \frac{1}{2}k. \quad . \quad . \quad . \quad . \quad . \quad (13)$$

This is the condition hinted at. It will be applied numerically in each of the cases to be treated presently. As to the sign of the square root it will be easily decided, remembering that both σ and b_0 are essentially positive. Thus, b , g , and therefore k , being known from observation, the product σb_0 will be found. Inserting this in (8) we shall find the atomic coefficients g_0 , b_0 , and therefore also σ and the interatomic distance.

Finally, the condition of stability is (*loc. cit.*, p. 115),

$$\gamma_0 > \frac{B}{2\pi R^3}, \text{ i. e. } \frac{B\sigma}{\alpha} < \frac{4\pi^2 c^2}{\lambda_0^2},$$

that is, in terms of b_0 , by formula (5),

$$\sigma b_0 < 1. \quad . \quad . \quad . \quad . \quad . \quad (14)$$

This necessary and sufficient condition of optical stability will be tested in each of the particular cases to which we shall now pass.

Hydrogen.

The observed values of refractivity of hydrogen gas at 0° C. and pressure 760 mm. are, for the lines H_α , D , H_β , and H_γ respectively,

$$\mu - 1 = 1.387 \quad 1.392 \quad 1.40_6 \quad 1.412 \cdot 10^{-4}.$$

The molecular weight of hydrogen gas (H_2) is $M = 2.016$, and its density, at the above temperature and pressure, $d = 8.9873 \cdot 10^{-5}$. Whence the corresponding values of the molecular refractivity,

$$N = \frac{\mu^2 - 1}{\mu^2 - 2} \frac{M}{d} \div \frac{2}{3} (\mu - 1) \frac{M}{d},$$

$$N = 2.074 \quad 2.082 \quad 2.10_3 \quad 2.112.$$

These observed values can be represented with sufficient accuracy by

$$N = 2.044_5 + \frac{.01279}{\lambda^2}, \lambda \text{ in microns.}$$

In fact, the latter formula gives, for H_α , D , H_β , H_γ , respectively, 2.074, 2.081, 2.099, 2.112. Thus, in c.g.s. units,

$$b = 2.044_5; \quad g = 1.27_9 \cdot 10^{-10}, \quad . \quad . \quad . \quad (H_2)$$

in the visible region of the spectrum at least. Whence the required ratio

$$k = b^2/g = 3.268 \cdot 10^{10},$$

i. e. $\frac{1}{2}k = 1.634 \cdot 10^{10}$. Now $\epsilon = 1.83 \cdot 10^{10}$. Thus the smallest

integer satisfying the condition (13) is $\kappa=1$. Consequently we shall attribute *one* dispersive electron to each hydrogen atom, *i. e.* put

$$k_0 = \epsilon = 1.83 \cdot 10^{10} \quad , \quad . \quad . \quad . \quad . \quad (H)$$

Introducing these values of k , k_0 into formula (12) we find (as the unique positive root)

$$\sigma b_0 = 0.4932 \quad . \quad . \quad . \quad . \quad . \quad (15)$$

Thus the condition of stability, (14), is amply satisfied. Substituting this value of σb_0 , and the above b , g for H_2 in (8), we find, for the atomic coefficients of hydrogen,

$$b_0 = 0.7719; \quad g_0 = 0.325_5 \cdot 10^{-10} \text{ c.g.s.} \quad . \quad . \quad (16)$$

Thus the atomic refractivity N_0 of hydrogen, which may conveniently be denoted by H itself, will be

$$H = 0.7719 + \frac{.00326}{\lambda^2} (\lambda \text{ in microns}) \quad . \quad . \quad (16a)$$

Notice in passing that the free wave-length $\lambda_0 = \lambda_H$ belonging to a hydrogen atom is equal $(g_0/b_0)^{1/2}$, by (5), that is, by (16),

$$\lambda_H = 6.494 \cdot 10^{-6} \text{ cm.} = 649.4 \text{ \AA.U.}, \quad . \quad . \quad (17)$$

much beyond the Lyman region.

Applications of the above atomic refractivity of hydrogen will be given at a later opportunity. In the present note I should like to draw the reader's attention chiefly to the interatomic distance which follows from the above results. From (15) and the first of (16) we have $\sigma = \alpha/2\pi R^3 = 0.6389$, where $\alpha = 4.88 \cdot 10^{-24}$. This gives for the central distance of the two atoms in a molecule of hydrogen

$$R = 1.067 \cdot 10^{-8} \text{ cm.} \quad . \quad . \quad . \quad . \quad . \quad (18)$$

Now, the remarkable thing about this distance is that it approaches very nearly the values of the semidiameter of a molecule of hydrogen (considered as an elastic sphere), obtained by various methods based on the kinetic theory of gases. In fact, these values are *,

| | Deviation from Boyle's Law. | Viscosity. | Heat- conduction. | Diffusion. |
|----------------|--------------------------------|------------|----------------------|----------------------------------|
| Semidiameter = | 1.025 | 1.024 | 0.995 | $1.01 \cdot 10^{-8} \text{ cm.}$ |

If we were to judge from this single case the coincidence could claim to be one of the order of magnitude only. But the following two cases, of oxygen and nitrogen, will show that there is more than this.

* Cf. J. H. Jeans's 'Dyn. Theory of Gases,' p. 340 (1904).

Oxygen.

Determining the coefficients b , g from the observed refractivities $\mu-1$ of oxygen gas for the lines H_α , H_γ , which, at normal temperature and pressure, are 2.697 and $2.747 \cdot 10^{-4}$, I find, with $M=32$ and $d=1.4294 \cdot 10^{-3}$,

$$b=3.967; \quad g=2.50 \cdot 10^{-10}, \quad . \quad . \quad . \quad (O_2)$$

whence

$$k=b^2/g=6.297 \cdot 10^{10},$$

i. e. $\frac{1}{2}k=3.149 \cdot 10^{10}$. Thus the smallest integer fulfilling the condition (13) is, in the present case, $\kappa=2$ (which happens to coincide with the "valency" of oxygen). Consequently we shall attribute *two* dispersive electrons to each oxygen atom,

$$k_0=2\epsilon=3.66 \cdot 10^{10}. \quad . \quad . \quad . \quad . \quad (O)$$

Substituting these values of k and k_0 in (12), we have

$$\sigma b_0=0.5446, \quad . \quad . \quad . \quad . \quad . \quad (19)$$

again satisfying amply the condition of stability (14). This value, together with the above b , g for O_2 , substituted in (8) gives, for the atomic coefficients of oxygen,

$$b_0=1.418; \quad g_0=0.5497 \cdot 10^{-10}, \quad . \quad . \quad . \quad (20)$$

and for the free wave-length belonging to an oxygen atom

$$\lambda_0=6.226 \cdot 10^{-6} \text{ cm.} = 622.6 \text{ \AA.U.} \quad . \quad . \quad . \quad (21)$$

From (19) and the first of (20) we have $\sigma=0.3840$, whence, the distance of the two atoms in a molecule of oxygen,

$$R=1.265 \cdot 10^{-8} \text{ cm.} \quad . \quad . \quad . \quad . \quad (22)$$

This again coincides with the semidiameter of the oxygen molecule*, as found by the methods of the kinetic theory of gases, viz.:

| Viscosity. | Heat-conduction. | Diffusion. |
|------------|------------------|----------------------------------|
| 1.405 | 1.29 | $1.35 \cdot 10^{-8} \text{ cm.}$ |

In this case the distance R differs from the heat-conduction value even much less than this does from the viscosity and the diffusion value of the semidiameter.

Nitrogen.

The observed refractivities for nitrogen gas (N_2) at normal conditions are 2.982 and $3.020 \cdot 10^{-4}$ for the lines H_α and H_γ respectively; $M=28.02$, $d=1.2507 \cdot 10^{-3}$. Proceeding as in the former case, I find from these data

$$b=4.409; \quad g=1.91 \cdot 10^{-10}; \quad k=\frac{b^2}{g}=10.20 \cdot 10^{10}, \quad (N_2)$$

i. e. $\frac{1}{2}k=5.10 \cdot 10^{10}$. The smallest integer, therefore,

* As it should do if, say, the spherical atoms are in contact with one another. It will be remembered that R is the mutual distance of the "centres" of the atoms.

XX. *A Note on Radiation.* By R. H. KENT, *Instructor, Department of Electrical Engineering, University of Pennsylvania* *.

ATTENTION should be drawn to a fundamental fallacy in the deduction of Kirchhoff's law for radiation. To deduce it, it is necessary to establish the proposition that there is no net transfer of energy by radiation across the boundary of two abutting media when they are at the same temperature, or that the radiant energy transmitted across the boundary in unit time in one direction is equal to the amount transmitted in the opposite direction. The reasoning by which this proposition is established is as follows:—

From the equality of temperature of the two media it is correctly inferred that there is no total net transfer of energy across the boundary. It is next assumed that transfers of energy due to temperature differences are accomplished in two ways, by radiation and by conduction, and, moreover, it is tacitly assumed that the process of conduction involves no energy transfer by radiation. Then, since there is no temperature gradient, it is correctly inferred that there is no net transfer by conduction, and hence (in view of the fact that the total net transfer is zero) that there is no net transfer by radiation, which is the proposition to be established.

The fallacy referred to consists in the tacit assumption that the process of conduction involves no energy transfer by radiation. Now conduction in the sense used in the deduction of Kirchhoff's law is a net energy transfer, the rate of which is proportional to the vector temperature gradient. Such an energy transfer may conceivably, and in all probability does, involve a transfer of energy by radiation from molecule to molecule of the conducting substance, which in certain cases may fail to vanish with the temperature gradient. In general, for example in the interior of a homogeneous isotropic body, it is likely that the radiation part of the energy transfer involved in conduction vanishes with the temperature gradient, but across the boundary between two different media it is easily conceivable that this is not the case. That is to say, it is not unlikely that across the boundary between two media at the same temperature there should flow an energy current in one direction conveyed by impacts and in the opposite direction an equal energy current of radiation.

* Communicated by the Author.

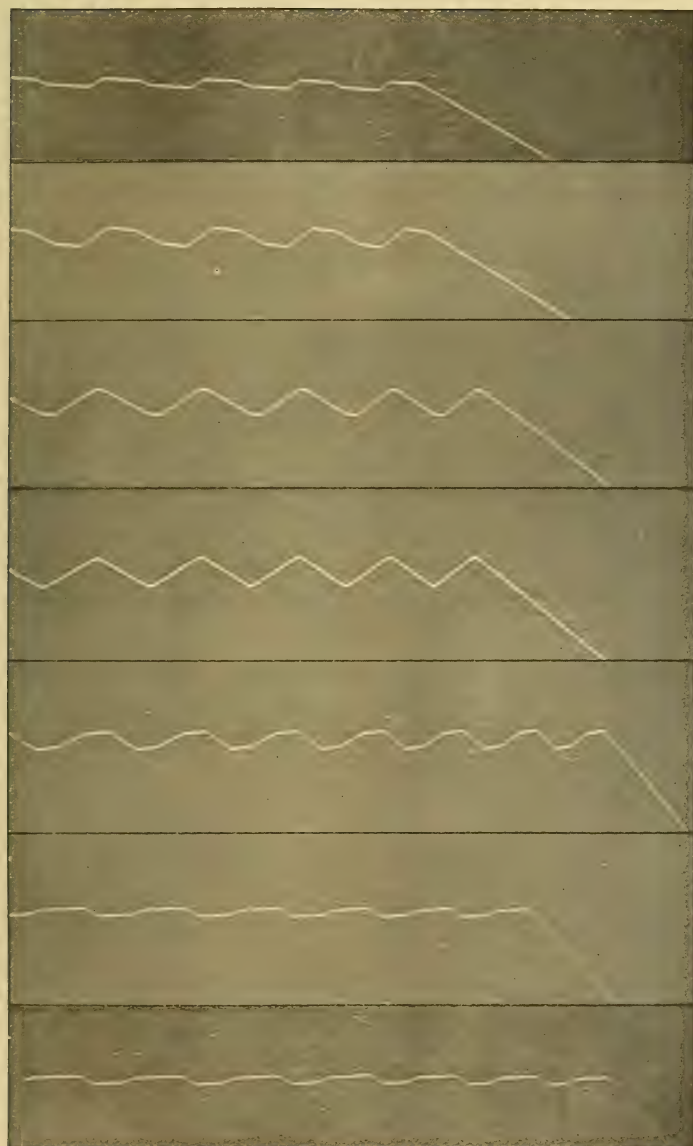
Accordingly conduction and radiation do not refer to mutually exclusive classes of phenomena, and hence from the absence of energy transfer by conduction and from the fact that the total net energy transfer is zero, the absence of net energy transfer by radiation cannot be deduced.

It is easy to see how such confusion could have arisen. Most of our ideas of conduction depend on the observation of phenomena at temperatures at which no radiation is visible. Hence, conduction has come to connote absence of energy transfer by radiation, although no such absence is implied in the definition of conduction here and commonly used. Formerly the conduction of heat was conceived as a flow, and as such was regarded as entirely distinct from the transfer of heat by radiation. But since the rise of the modern molecular and electronic theories such a conception can no longer be considered adequate. The conduction of heat is effected not only by what may be loosely termed molecular and electronic impacts, but also by radiation from molecule to molecule.

This note has been written with no quibbling intent, but with a view seriously to contest the thermodynamic foundations of Kirchhoff's law. A consideration of the state of affairs when two abutting media are at the same temperature may make the situation clearer. Energy may be transmitted across the boundary in two ways, by molecular and electronic impacts and by radiation. From thermodynamic considerations alone it is impossible to show that the net energy transfers in these two ways are separately zero; all that can be thus legitimately deduced is that the rate of transfer by one of these means is equal and opposite to the rate of transfer by the other. An attempt might be made to demonstrate the absence of net impact transfer by kinetic theory. But in view of the well-known failure of the law of the equipartition of energy—in particular, the fact that the molecules of a metal at a low temperature do not possess the same mean kinetic energy of translation as the molecules of a gas in contact with it and at the same temperature might be given as a pertinent instance of this—such reasoning would lack cogency. That Kirchhoff's law as an empirical fact *may* be true is, of course, not questioned. If such is the case, it is likely that it is the consequence of a fundamental similarity in the radiating mechanisms of all substances.

My views on this subject owe such clearness as they possess to several conversations with Dr. H. M. Trueblood, of the Department of Electrical Engineering of the University of Pennsylvania.

FIG. 2.

Observed
at

1/9

1/4

27.5

1/2

3/4

8/9

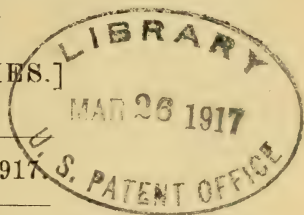
8/9

Photographs of vibration-curves showing the initial motion and the subsequent vibration with discontinuous changes of velocity.

THE
LONDON, EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

[SIXTH SERIES.]

MARCH 1917.



XXI. *On the Positive Ionization from Certain Hot Salts, together with some Observations on the Electrical Properties of Molybdenite at High Temperatures.* By A. T. WATERMAN, *Princeton University* *.

THE general problem as to the character of the ionization from hot bodies has been examined in considerable detail during recent years. The results obtained from experiments with metallic strips indicate, on the whole, no characteristic emission, but one which is apparently the same for all the metals and due no doubt, so far as the positive emission is concerned, to some common impurity. The positive emission is now generally considered to consist mainly of potassium atoms with a single charge ; the negative of electrons.

From experiments with various salts the following general conclusions have been reached, although there are exceptions :—

- I. Positive emission : characteristic of the metallic constituent.
- II. Negative emission : electrons accompanied in some cases by an emission characteristic of the remaining constituent.

The metals whose salts (chiefly the halides and sulphates) have been investigated are :—

Alkaline group : K, Na, Li, Rb, Cs.

Alkaline-earth group : Be, Mg, Cd, Zn, Sr, Ca, Ba ;

and

Al, Mn, Fe.

* Communicated by Prof. O. W. Richardson, F.R.S.

Phil. Mag. S. 6. Vol. 33. No. 195. March 1917.

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Of these the Zn and Cd halides give a positive emission consisting of doubly charged atoms.

Mn and Al vary considerably in their emission, so that nothing very definite can be said about them.

Be and Fe apparently give only the K-impurity emission like that from the pure metals.

All the rest yield a positive emission consisting of singly charged atoms of the metal.

The question naturally arises as to the reason for obtaining a singly charged ion in some cases and a doubly charged in others. This does not appear to be connected simply with the valence as might be expected. In other words, how can one predict what the emission from a given salt will be? The experiments that follow were instituted with a view to attempting an answer to this question. Only positive emission was considered and a number of salts were tried, the metals of which differed in valence.

The following were the salts employed :—

| | |
|---------------------------------------|----------------------------------|
| AgCl | Cu ₂ Cl ₂ |
| AgBr | AlF ₃ |
| PbCl ₂ | PtCl ₂ |
| PbBr ₂ | |
| CuCl ₂ . 2H ₂ O | MoS ₂ (mineral form). |

Method.

The method employed was identical with that used by Prof. Richardson in his article on "The Ions from Hot Salts," published in the *Phil. Mag.* for September 1913, pp. 452-472. Briefly, the salt is placed on a narrow strip of platinum whose emission has previously been driven out by continued heating to a temperature above which measurements with the salt are to be made. The salt is then heated by passing a current through the strip, and the temperature roughly ascertained from the resistance of the strip. If now the strip is raised to a certain potential, emission from the hot salt is driven off. A magnetic field is then applied which deflects the stream of ions. The amount of this deflexion is taken when the magnetic field is reversed. This deflexion obviously depends on

1. The dimensions of the apparatus.
2. The potential applied.
3. The strength of the magnetic field.
4. The value of e/m for the ions.

The formula connecting these quantities is :

$$\frac{e}{m} = \frac{9}{2} \frac{Vx^2}{H^2d^4} * \dots \dots \dots (1)$$

where V = potential, H = strength of field, d = distance between strip and plate which receives ions, and x = half the deflexion caused by reversal of field.

All these quantities were measured as described in Prof. Richardson's article on "Positive Ions from Hot Metals" †.

The platinum strip was cut with narrow and short constrictions, one on each side of the centre. When a current was passed through, these constrictions would become hotter than the rest of the strip, and thus would tend to hold in place a salt lying between them.

The accuracy of the results of the experiment was found to depend upon the accuracy with which the distance d could be measured and kept constant. To accomplish this end two methods of mounting the strip were used :—

(a) A very short strip was made ; its ends were soldered to two heavy brass strips connected to the lead wires for the heating circuit. It was thought that the shortness of the strip would diminish the bending due to changes in temperature and hence length. This method was found to be not altogether satisfactory.

(b) A longer strip was used, fastened at one end rigidly to the end of one lead wire, and at the other to a phosphor-bronze spring acting as the other lead wire. This spring was under tension sufficient to take up any increase in length and to hold the strip level. When carefully adjusted this mounting was very successful.

The making and successful mounting of a perfect strip is rather a delicate operation. This, together with the inevitable subsequent variations in the distance d and many other difficulties, made an exact experiment a tedious process.

The temperature-resistance curve of a test Pt strip in air was drawn by taking the following as fiducial points :—

- Room temperature.
- Boiling water.
- Melting point of NaNO_3 .
- " " " Borax.
- " " " Na_2SO_4 .

* Richardson, Phil. Mag., Nov. 1908, p. 740.

† Roy. Soc. Proc. A. vol. lxxxix. p. 507 (1914).

The graph was a perfect straight line as nearly as could be seen. Knowing the resistance at room temperature of the strip actually used in the experiment, the same fiducial points could be calculated for it and a similar temperature-resistance curve obtained. From these the temperature of the strip could be inferred from its resistance with a fair degree of approximation. The actual resistance of the strips used when cold varied from $\cdot 3$ to $\cdot 8$ ohm.

The method of measurement was chiefly the "balance," method as defined by Richardson*, but readings by the "slit" method were taken whenever feasible.

The pressure in the tube in which the strip and connexions were enclosed was always less than 10^{-4} mm. of mercury.

In the tables that follow, m/H is the ratio of the mass of the ion to that of an H-ion in electrolysis on the supposition that it carries an equal charge. The charge of an H-ion was taken to be 9649 electromagnetic units. B and S refer to the "balance" and "slit" methods of measurement respectively.

1. *Silver Chloride.*

(a) The first specimen used was probably fairly pure, but it was considerably darkened by exposure. A very small amount was moistened with distilled water and placed on the strip, mounted by method (a). The emission from the strip had been driven out for all temperatures below 1000° C. Above this point considerable emission from the Pt would certainly be present.

The melting point of AgCl is given as 450° C. Permanent emission was first detected at about 400° , but was at that point too small to admit of measurement.

| V. | H. | Method. | Temperature. | Mean values. | |
|-----|------|---------|-------------------|--------------|---------|
| | | | | e/m . | m/H . |
| 160 | 1487 | B & S | 460° | 254.4 | 37.9 |
| | | | to 1100° | | |

The values for e/m were quite consistent—within about 3 per cent. variation from mean—and some forty readings were taken.

(b) Another specimen of the same salt was placed on the strip under the same conditions, giving the following results:—

| V. | H. | M. | T. | e/m . | m/H . |
|-----|------|-------|------------------|---------|---------|
| 140 | 2030 | B & S | 465° | 259.8 | 37.1 |
| | | | to 940° | | |

* Phil. Mag., Sept. 1913, p. 453.

This value for e/m is the mean of thirty readings in even better agreement than in the previous case.

(c) An attempt was made to see whether freshly prepared AgCl would yield the same results. This specimen was prepared from the purest AgNO₃ and HCl obtainable, and kept as far as possible from the light. The salt was precipitated in the form of heavy white flakes, and the greatest difficulty was found in keeping the salt on the strip when it was heated.

A fresh strip of Pt was inserted and measurements were taken on its emission to check the accuracy of the later experiments with AgCl. It was glowed until no appreciable emission was detected below 1250° C. It was mounted by method (b).

| V. | H. | M. | T. | e/m . | m/H . |
|-----|------|-------|----------------------|---------|--|
| 203 | 2460 | B & S | 1000° to 1120° | 247·5 | 38·9 dry salt. |
| 203 | 2460 | B | 790° to 1130° | 244·6 | 39·4 moistened with distilled H ₂ O. |

These values were the mean of a number of readings as consistent as the former.

(d) Silver Iodide. This salt was furnished by Eimer & Amend with no specifications as to its purity. A Pt strip, mounting (b), was used on which PtCl₂ had previously been tested, but which had been glowed for points below 1200° C.

The melting point of AgI is given as 527° C. The initial emission was looked for with extreme care, and the first signs of it appeared at 520°. It was far too small to measure, and died away very quickly. A definite emission was found at 575°.

| V. | H. | M. | T. | e/m . | m/H . |
|-----|------|-------|---------------------|---------|---------|
| 204 | 2460 | B & S | 650° to 1195° | 267·3 | 36·2 |

These values, about twenty in number, of which these are the mean, were also very consistent although slightly lower than the preceding for AgCl. The difference is probably due to the distance d varying.

Conclusion.—The values here given for m/H for AgCl and AgI do not point to any characteristic silver emission which can be detected, the atomic weight of Ag being 107·88. The numbers were quite consistent and averaged a little lower than the K impurity emission from metals, for which $m/H = 39$.

Furthermore, the readings could only be taken at temperatures for which at such low pressures the salt must have been vaporized. If an impurity were present of low volatility, *e. g.* the common salts of potassium, it would remain on the strip and become active.

In cases (a) and (b) considerable metallic silver was known to be present. In (c) the distilled water alone would be enough to account for an emission at 800° and over (see § 6).

2. Cuprous Chloride.

(a) The first specimen was made by Kahlbaum, but the salt had been exposed to the air for a long time, so that it was light green in colour, due no doubt to partial oxidation to CuCl_2 . The salt was deposited dry on a Pt strip, of mounting (a), which had been glowed up to 1000°C . The melting point of Cu_2Cl_2 is given as 434°C .

| V. | H. | T. | M. | <i>e/m</i> . | <i>m/H</i> . |
|-----|------|----------------|----|--------------|--------------|
| 156 | | 533° | | 358.0 | 27.0 |
| & | 1487 | to | B | to | to |
| 168 | | 1100° | | 311.6 | 31.0 |
| 156 | 1487 | 530° | S | 413.0 | 23.35 |
| | | | | 392.8 | 24.55 |
| | | | | 392.0 | 24.6 |
| | | | | 405.0 | 23.8 |
| 168 | 1487 | 1000° | S | 376.8 | 25.6 |
| | | | | 387.4 | 24.9 |
| | | | | 311.6 | 31.0 |

From a single curve

The values of *m/H* by the balance method rose steadily from around 27 at 530° to about 31 at 1000° and remained there. The only distinct values obtained by the slit method are given above. They appear to be due to Na impurity —*m/H* = 23—at the lower temperature. At the higher the Na^+ value still continues with one reading of a possible Cu^{++} ion. There is evidently more than one kind of ion involved.

(b) A pure sample of Cu_2Cl_2 was used for this experiment, —Kahlbaum's "zur Analyse." It was placed on a Pt strip, mounted by method (b), which was used for experiments with PtCl_2 and AgI , but which had been glowed for points below 1100°C . The salt was white and semi-transparent.

| V. | H. | M. | T. | <i>e/m</i> . | <i>m/H</i> . |
|-----|------|-------|----------------|--------------|--------------|
| | | | 870° | | |
| 205 | 2460 | B & S | to | 280 | 34.4 |
| | | | 1200° | | |

About twenty readings were taken, which ran from about 35 at 900° to 32·5 at 1100°. The few readings taken by the slit method gave values around 32·5, except one at 900°, the only one taken below 1100°, which gave 35·9.

Conclusion.—From these values of m/H it certainly would seem as if a Cu^{++} ion had been detected. The first specimen (a) evidently was not at all pure, but there were signs of a doubly charged ion at high temperatures. When emission first set in with (b) the values were uncertain. At the higher temperatures there are still more positive evidences of a Cu^{++} ion, for which $m/H = 31·6$.

In any case there is probably no emission of Cu-ions under 1000° or so. At this temperature and pressure, however, the salt must long since have been vaporized. If there is an emission of Cu-ions then, it seems likely that it must come from the action of the Pt on the vapour. This was shown to be possible by Sheard*.

Cupric Chloride : $\text{CuCl}_2, 2 \text{H}_2\text{O}$.

(c) This salt was probably very pure—Kahlbaum, kryst, “zur Analyse.” Its melting point is 498° C. At 100° CuCl_2 with water of crystallization loses half its chlorine to form Cu_2Cl_2 . This action was confirmed.

The Pt strip, mounting (b), on which measurement was made had been glowed below 1100°. Emission from the salt was first detected at 780°. A great deal of trouble was experienced in keeping it on the strip when dry.

| V. | H. | M. | T. | e/m . | m/H . |
|-----|------|-------|-------------|---------|--------------------|
| | | | 840° | | |
| 204 | 2460 | B & S | to 1200° | 266·3 | 36·3 dry crystals. |
| | | | 870° | | |
| 204 | 2460 | B | to 1050° | 266·3 | 36·3 „ „ |

Conclusion.—This does not seem to be anything more than the regular impurity emission. The value is, however, a little low. As CuCl_2 is supposed to go over into Cu_2Cl_2 at 500°, this may be taken as evidence that the emission from Cu_2Cl_2 in (a) and (b) above is not characteristic Cu emission, but a combination of K and Na impurities for instance. Nevertheless, it is difficult to ascribe the very distinct values about 32 to an increase in the distance d . 32 as a low value for 39 is perhaps possible but not probable. It may thus be that the value 36·3 in (c) was due to a mixture of Cu^{++} and K^+ ions. In that case a characteristic Cu^{++} emission would take place in both cases. At all events there certainly is no sign of a singly charged ion of Cu.

* Phil. Mag., March 1913, p. 370.

3. *Lead Chloride.*

(a) The salt used for this test was primarily very pure, but it had undergone considerable exposure to the air. Its melting point is 500° .

The salt was moistened with distilled water and placed on the same strip, mounting (a), on which Cu_2Cl_2 and AgCl had been heated. The strip gave no significant emission below 1000° .

Emission was first detected at 460° , but it was too small for measurement and almost immediately died away. No emission was then found until 600° . This steadily increased with rise in temperature and readings were taken at 820° . The increase of emission with temperature was much less than with any of the other salts.

In making observations with the slit method when the emission was fairly large, curves were found with more than one maximum. In this case it seemed probable that this arose from different parts of the salt emitting rather than from there being more than one kind of ion present in any quantity. This was concluded partly from the shape of the curves; partly from the fact that the balance method gave results that were fairly steady; and from the fact that the values of m/H , calculated for a possible two kinds of ions (there being two distinct maxima), seem very unlikely. For instance, in a typical curve, the ions would have to be

$$m/H = 18.6 \quad \text{and} \quad m/H = 357.5$$

on this supposition.

The mean values for twenty readings follow:—

| V. | H. | M. | T. | e/m . | m/H . |
|-----|------|-------|---------------|---------|---------|
| 170 | | | 820° | | |
| 203 | 2030 | B & S | to | 259.9 | 37.0 |
| | | | 940° | | |

The balance method gave results varying from 35.5 at first to 39 at higher temperatures. The slit method, if interpreted as above, gave about 39.

Lead Bromide.

(a) This salt was of about the same purity as the PbCl_2 just described. Its melting point is 400° . It was moistened with distilled water and placed on the strip just used for PbCl_2 . The emission from the strip was negligible below 925° .

First signs of emission from the salt occurred at 400° , but soon died out. A fairly permanent emission appeared at 470° . The following mean values were obtained:—

| V. | H. | M. | T. | <i>e/m.</i> | <i>m/H.</i> |
|-----|------|-------|---------------------------------------|---------------------|-------------|
| 112 | 2030 | B & S | 530° to 1130° | 264.3 | 36.5 |
| 202 | 2030 | B & S | 460° to 490° | 254.4 fresh salt | 37.9 |

The balance and slit methods were in good agreement.

(b) The same PbBr_2 was used for this determination. A different Pt strip was employed on which AlF_3 had been heated. The emission from the strip was not comparable with that from the salt up to 1150° . The salt was put on with distilled water and the emission watched for very carefully.

Emission so very slight as almost to 'escape attention started at 100° , reaching a maximum at 400° , and then dropping to zero. Permanent definite emission set in at 560° and reached a measurable value at 660° . The strip was mounted by method (b) and the values were therefore much more consistent, agreeing within 1 per cent. almost all the time:

| V. | H. | M. | T. | <i>e/m.</i> | <i>m/H.</i> |
|-----|------|-------|---------------------------------------|-------------|-------------|
| 204 | 2460 | B & S | 690° to 1075° | 278 | 34.7 |

Conclusion.—The values of *m/H* for PbCl_2 and PbBr_2 are fairly consistent. There is no evidence of an emission characteristic of the Pb, for which it might be expected $m/H=103.5$.

The values seem quite evidently to be due to K as an impurity, although at times they are rather low.

It is possible that a characteristic emission of Pb was obtained in the last experiment with PbBr_2 , namely, the very slight emission detected from 100° to 400° . It was, however, far too slight for measurement.

4. Aluminium Fluoride.

Only one experiment was made with this salt, the specimen used being made by Kahlbaum. The melting point of AlF_3 is probably about 150° .

The salt was moistened with distilled water and placed on a new strip from which the emission had been driven out below 900° . The mounting was by method (b).

Emission from the salt was first detected at 150° , although here it was barely noticeable and soon passed away. At 620° it admitted of measurement. Some thirty readings were taken, as follows :—

| V. | H. | M. | T. | e/m . | m/H . |
|-----|------|----|---------------------|-------------|----------|
| 204 | 1000 | B | 660° | 175.5 | 55 |
| | | | to 840° | to 224.7 | to 43 |
| " | " | S | 740° | 241.2 | 40.0 |
| | | | | 232.6 | 41.4 |
| " | " | " | 815° | 225.2 | 42.8 |
| | | | | 212.3 | 45.4 |
| " | " | " | 830° | 211.8 | 45.5 |
| | | | | 223.5 | 43.2 |

The values by the balance method at first ranged around 55, coming steadily down as the temperature increased to 43° .

Conclusion.—The values for Al^{+} , Al^{++} , and Al^{+++} would be $m/H=27.1$, 13.5 , and 9 , respectively, so that there is apparently no Al emission at the above temperatures. Judging by the very low boiling-point the salt could only be in a state of vapour, and the emission above could be accounted for, in part at least, by the distilled water (see § 6). It is evident that the K emission is present, but whether the high values by the balance method are caused by the presence of some heavy ion or are due to the motion of the strip is a matter of doubt.

It is unfortunate that the initial emission beginning with 150° was too small and transient to measure.

5. Platinum Chloride.

(a) This salt was made by dissolving some clean strips of platinum in aqua regia. The solution was evaporated to dryness and the residue dissolved in distilled water. The washing process was repeated a number of times. Glass vessels were used throughout. A drop of the solution was finally placed upon the Pt strip, mounting (b), which had previously been used for AlF_3 and $PbBr_2$. The strip was glowed for temperatures below 1150° .

Emission was first detected at 550° and was measurable at 600° . It appeared to decay very rapidly, and measurements were first made at 720° .

| V. | H. | M. | T. | e/m . | m/H . |
|-----|------|----|----------------|---------|---------|
| 204 | 2460 | B | 723° | 268 | 36 |
| | | | to | to | to |
| | | | 945° | 358 | 27 |
| | | | to | to | to |
| | | | 1100° | 284 | 34 |

The values, some forty in number, decreased steadily with rise in temperature, and slightly with time at constant temperature, from 36 to 27, and then rose with increasing temperature to 34. The values by the slit method did not go lower than 30, but observed the same decrease and later rise.

(b) As the PtCl_2 used in the above determination was made in a glass vessel, and as glass is known to be quite soluble in aqua regia, a further quantity of PtCl_2 was prepared in a platinum crucible, so as to be more completely rid of this impurity. This does not remove it altogether, however, as glass is soluble to a slight degree in the HCl used. About sixty readings were taken :—

| V. | H. | M. | T. | e/m . | m/H . |
|-----|------|----|-------|---------|---------|
| 204 | 2460 | B | 780° | 256.1 | 37.6 |
| | | | to | to | to |
| | | | 945° | 264.3 | 36.5 |
| | | | to | to | to |
| | | | 1130° | 256.5 | 37.5 |
| „ | „ | S | 930° | 256.1 | 37.6 |
| | | | to | | |
| | | | 1100° | | |

The values were remarkably consistent and did not show any appreciable decrease until after long heating at 930°.

Conclusion.—No emission was found characteristic of Pt, unless it be taken as significant that PtCl_2 and a Pt strip give practically the same value of m/H . At any rate there appears to be no connexion with the atomic weight of platinum.

The presence of glass as an impurity would warrant the lowering of m/H due to Na compounds contained. That this is the case becomes more plausible when in (b) precautions are taken to keep the glass out as far as possible. The same decrease occurs but to a much less degree.

The emission seems to be without doubt due to K as an impurity.

6. Sources of Impurities.

As has already been touched upon, it is well known that a Pt strip, in fact apparently any strip of metal, no matter how carefully it is cleaned, gives off a decided positive emission when heated. It is quite persistent and does not appear to be characteristic of the metal, but may most probably be due to potassium in some combination as an impurity.

Now it has been shown * that a Pt strip which had lost

* Horton, Roy. Soc. Proc. A. vol lxxxviii. p. 131 (1912).

its power of emitting would regain it to some extent if heated in air. Several attempts have been made here to determine just how much this source of impurity entered into the ordinary manipulation of the apparatus.

A Pt strip was glowed until it showed no emission whatever below 1000° . The intensity of the emission was taken at 1150° , and the strip was allowed to cool in the vacuum. Dry air was admitted for one minute and immediately pumped out again. A reading of the emission was taken at the same temperature as before. The same thing was done after exposing the strip to cold dry air for 25 hours. Then the strip was removed and placed in a box for 42 days, exposed to the ordinary air in the room, and a reading taken again. The readings are given for the velocity of the electrometer spot in decimetres per second.

Then the same strip was tested in the same manner, being touched between readings with the Pt wire used to place the test salts on the strip. The wire always previously gave a negative flame test.

A further trial was made, placing a drop or two of distilled water on the strip between readings.

The results follow :—

| | Time. | | T°. | Intensity of | Remarks. |
|-----------------|-------|------|----------------|--------------|----------|
| | hrs. | min. | C. | emission. | |
| Pt strip alone. | 0 | 0 | 1150° | ·290 | |

Cold dry air admitted for one minute.

| | | | | |
|---|---|----------------|------|----------|
| 0 | 1 | 1150° | ·320 | Decaying |
| 0 | 4 | " | ·303 | fast. |
| 0 | 6 | " | ·279 | Fairly |
| 0 | 8 | " | ·275 | steady. |

Air admitted for 25 hours.

| | | | | |
|----|----|----------------|------|-----------|
| 25 | 8 | 1150° | ·376 | Decaying. |
| 25 | 13 | " | ·351 | |
| 25 | 18 | " | ·336 | Fairly |
| 25 | 28 | " | ·324 | steady. |

Exposed to air for 42 days.

42 days 805° ·161

(See measurement (A) of e/m here.)

| | hrs. | min. | C. | Intensity. | Remarks. |
|-----------------|------|------|----------------|------------|-------------|
| Pt strip alone. | 0 | 0 | 1050° | ·01 | Increasing. |
| | 0 | 5 | " | ·200 | Steady. |

Distilled water placed on strip with Pt wire.

| | | | |
|---|----|---------------|------|
| 0 | 8 | 725° | ·01 |
| 0 | 11 | 870° | ·45 |
| 0 | 14 | 930° | 2·50 |

(See measurement (B) of e/m here.).

When touched by a Pt wire between readings the emission at 1150 was increased only 10 per cent., which can be accounted for simply by the exposure to the air in taking out the strip.

The distilled water was made in a block tin vessel and kept in a bottle washed repeatedly with distilled water, but not boiled. It was the same water which was used in laying the various salts on the Pt strip in the previous experiments.

Measurements on m/H from the strip (see above) :

| (A) | V. | H. | M. | T. | m/H . | |
|-----|-----|------|----|-------|---------|--------------------------------------|
| | 203 | 2460 | B | 1027° | 40.1 | Pt strip after long exposure to air. |
| | " | " | " | 1090° | 36.7 | |

Strip glowed out to 1100°.

| (B) | V. | H. | M. | T. | m/H . | |
|-----|-----|------|----|------|---------|--|
| | 204 | 2460 | B | 930° | 37.7 | Strip plus distilled H ₂ O. |
| | " | " | " | 933° | 36.7 | |

From these investigations of the sources of impurities in handling the apparatus it appears that the salts which it was possible to mount on the strip dry were practically uncontaminated, as far as the process of mounting went. The only chance for impurity not already in the salt would be a very slight amount from exposure to the air.

As for the salts mounted with water, if no emission below 800° could be obtained sufficient to take readings, the chances are that the emission from the water would figure largely in the results. By emission from the water of course emission from impurities brought in with the water is meant. If emission was obtained at temperatures below 700°, it is likely that the emission due to the water would not enter into the results.

A very noticeable characteristic of these impurities is that they are not at all lasting. The decay was found to be quite rapid for every case except the one where the Pt strip was exposed to the air for 42 days. In this case the emission was found to increase considerably at constant temperature for a short time after heating was begun.

7. *Molybdenite.*

This mineral appeared to be well adapted for measurements with this apparatus. It occurs in the form of flat sheets, rather soft, of a metallic lustre, and very sectile.

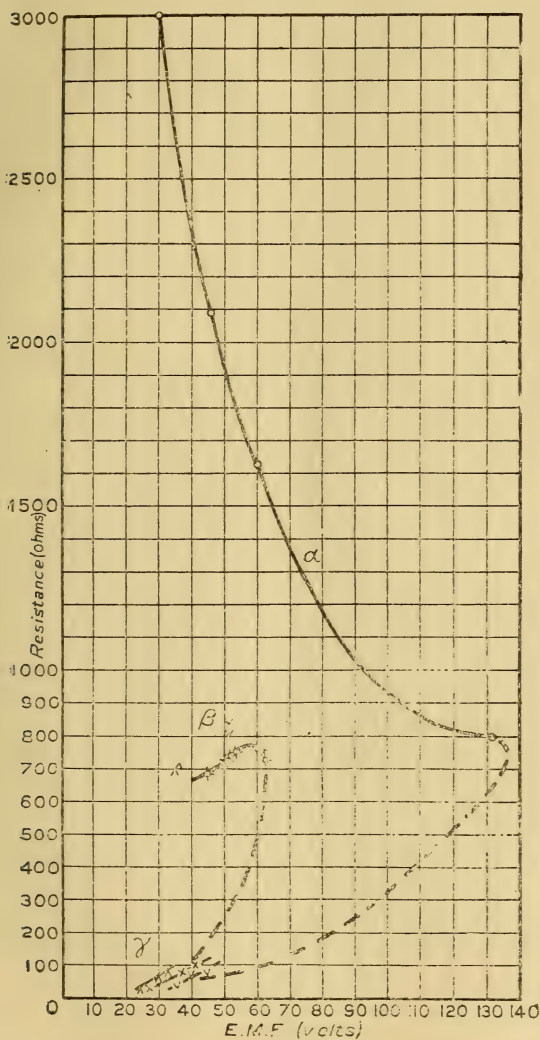
Strips are quite easily prepared for use. But it is not readily soldered. For this reason the method of mounting was changed somewhat, and two small brass screw clamps were employed to hold the ends of the strip. It was difficult to obtain a uniform contact for all variations in temperature, as on account of the softness of the mineral too much pressure could not be applied at the clamps without crushing the strip to a powder, whereas too little pressure meant serious instability of resistance. The surface of the strip was flush with the lower plate of the apparatus for measuring e/m when cool, but no arrangement was used to make certain that it was thus when hot. The thickness of the strips was about 1.5 mm., somewhat greater than that of the Pt strips used, otherwise the dimensions were practically the same.

The electrical conductivity of molybdenite presents peculiar and interesting features. With small applied potential differences the resistance of the strips is very high, but diminishes rapidly with increasing potential differences. No doubt this alteration in conductivity is partly due to the rise in temperature caused by the electric current, and is similar to the effects shown by a large number of minerals which have been examined in detail by Koenigsberger and Schilling*. The effect does not, however, appear to be entirely, or perhaps even principally, a temperature effect, since it is shown under very low voltages when the currents are too small to cause any perceptible increase in the temperature of the material. Thus with one strip the resistance was 8.1×10^5 ohms for 2 volts applied potential difference and 3.52×10^6 ohms for 0.1 volt. The diminution of resistance with increasing potential difference continues uniformly up to a certain potential difference, which varies to some extent with different specimens and according to the treatment to which they have been subjected; at this point, which will be referred to as "the break," the resistance diminishes suddenly and the mineral conducts, at a red heat, with a comparatively low resistance. Before the voltage has been raised sufficiently for the break to occur the resistance diminishes, as has been noted above, with increasing voltage, whereas after the break the resistance diminishes with diminishing voltage. This difference may be regarded as characteristic of two states, α and β , of the material which occur before and after the break. The phenomenon of the break is reversible, but the rate of change of state decreases after long heating. The substance also tends to persist in the state in which it was when the current was turned off.

* *Ann. der Phys.* vol. xxxii, p. 179 (1910).

For example, when, after passing through the break and turning off the current, gradually increasing potentials were

Fig. 1.



applied, the resistance was found to increase with increasing potentials up to a potential a little below that at which the break occurred. These relations are exemplified in fig. 1.

The portion (α) of the curve represents the initial heating before the break; the group of points (β) was taken after the break; the group (γ) was obtained after the strip had been heated for a long time in the second state. Lines are drawn connecting the definite consecutive readings. The dotted line represents the break or change in state. The portion (α) of the graph for low values of the potential has the form of approaching the vertical axis asymptotically; the value of the resistance for a potential difference of two volts was 40,100 ohms, for instance. Results of the same general character as those indicated were obtained with different strips, and when the resistances and potential differences were measured in a variety of ways.

As the break was approached the values of the resistance for a given potential were observed to decrease with time; so that often a considerable interval elapsed before the resistance reached a steady value. Beyond the break it was often difficult to maintain a steady resistance. The resistance of one of the strips under constant voltage was measured at 24° C., 100° C., 262° C., and 316° C. The break was found to occur at 310° C. Below the break the resistance varied with the absolute temperature T in accordance with the formula $Ae^{b/T}$, where A and b are constants. Normally molybdenum sulphide belongs to the hexagonal class of crystals, type dihexagonal equatorial. In the experiments the heating current was passed through the strips at right angles to the crystallographic " c " axis. There is no evidence of any change of crystalline or chemical structure at the break unless a sudden rise in temperature observed at that point can be so interpreted. The variation of resistance with current for very small currents and the tendency to persist in the second state, already alluded to, suggest that the electrons are liberated in the material, partly by the action of the electric field and not merely as a result of the increase of temperature. Apparently the best condition for a quick return from the second to the first state is the presence of a small current, but one which is not zero. Professor A. Trowbridge has shown that the sign of the Hall effect in molybdenite indicates that the current is carried by negative electrons.

8. *Emission.*

The first experiments to determine e/m , made by the method used in dealing with the salts as described in the

earlier part of this paper, gave very erratic results. It was felt that this might be caused by the drop of potential along the molybdenite strip owing to its high resistance. This makes the value of V to be substituted in the formula for e/m uncertain even when, as in most of the experiments, the potential is applied at the middle of the strip by means of a sliding contact to an external high resistance shunt. Even in this case the correct effective potential will only be that at the centre of the strip provided the emission is symmetrical about the centre. This difficulty might have been overcome by measuring the magnetic deflexions with the heating currents successively in opposite directions, but this method was not found to be practicable. The methods finally adopted were (1) heating the molybdenite strip directly by an alternating current, and (2) heating the molybdenite on an auxiliary strip of platinum.

On searching for a positive emission from the strip a very slight amount was observed in all cases when the strip was new at a point considerably below the break. This was transient and could not be measured. Permanent emission commenced just below or just at the start of the break, and it is here that measurements were commenced. The substance at red heat is very active in its emission, so that as the temperature was increased the sensitiveness of the electrometer had to be decreased by adding capacities to the pair of quadrants in order to get anything like accurate readings. Except in a few instances the balance method was the only one by which good results were obtained, as the substance was too erratic in its behaviour to give at all satisfactory curves. Other repeated attempts by the slit method failed, principally for the reason that constancy of resistance, and hence temperature, could not be maintained. Even when the temperature apparently remained constant there was often a sudden or a gradual shift in the location of the maxima. The measurements were all made in a mercury vacuum, with the McLeod gauge showing less than 5×10^{-5} mm. of mercury.

In the measurements of e/m the centre of the molybdenite strip was maintained at a fixed potential V_0 with reference to the opposite plates by means of a connexion from a high potential battery to a point between two megohm resistances in series shunted across the strip outside the apparatus. The strip was then heated by an alternating current obtained by the commutation of a direct current. The use of an alternating current makes the effective potential entering into

equation (1) equal to the potential V_0 at the middle of the strip, no matter what the fall of potential due to the heating current or what the distribution of emission of the ions along the strip may be. This may be shown by the following argument, for which I am indebted to Professor Richardson:—Imagine the strip to be represented by a vertical line AB and the deflexion caused by the magnetic field to occur in a horizontal direction. For given values of z , H , and e/m , the magnetic deflexion x is determined at each point by the value of the potential difference V between that point and the plates. Suppose that the strip lies along the y -axis and the intensity of emission between y and $y+dy$ is denoted by $f(y)dy$. Let the actual balance position for a given value of H be x_1 . Corresponding to x_1 there will, from equation (1), be a particular value V of the potential difference which will belong to a point C of the strip when the electric current is flowing in one direction, and in general, let us suppose, to some other point D when the current is flowing in the opposite direction. The condition for a balance is clearly

$$\int_A^C f(y) dy + \int_D^B f(y) dy = \int_A^D f(y) dy + \int_C^B f(y) dy$$

or

$$\int_D^C f(y) dy = 0. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

As $f(y)$ is necessarily positive, it follows that C and D are coincident, and as they have to have the same potential they must coincide with the only point whose potential V_0 is independent of the direction of the heating current. For this theory to hold the potentials at every point must be sufficient to saturate the emission current.

The alternating current actually used was obtained from a direct current by means of a rotating commutator with a frequency of about 20 cycles per second. This frequency was high enough for the electrometer readings to be sufficiently steady. It was not found possible to get readings actually in the break with this arrangement, as the molybdenite strip could not be induced to stay in the break. The measurements which follow were taken with very little preliminary heating,—only the amount necessary to take a series of readings of the resistance up to the start of the emission.

| Remarks. | M. | Current. | <i>r</i> . | <i>m/H</i> . |
|--------------------|----|----------|------------|--------------|
| Just before break. | B | D | 35500 | 86.9 |
| | | R | " | 39.5 |
| Direct Current. | | R | 35000 | 34.4 |
| | | D | 34850 | 43.2 |
| | | D | 34700 | 38.9 |
| | | R | " | 40.85 |
| | | R | 34670 | 40.0 |
| | | D | " | 42.6 |
| | S | D | 34400 | 35.95 |
| | " | D | 34200 | 40.55 |
| | B | D | 33720 | 42.45 |
| | | R | " | 40.9 |
| Commutated. | B | ... | >20000 | 39.0 |
| Direct current. | | | " | 46.7 |
| | | | " | 48.05 |
| Before break. | | | " | 44.1 |
| | | | " | 43.65 |
| | | | " | 49.1 |
| | | | " | 40.0 |
| | | | " | 29.06 |
| | | | " | 25.02 |
| | | | " | 29.8 |
| | | | " | 54.65 |
| | | | " | 40.4 |
| Break | | | | |
| | | | 3540 | 34.1 |
| In second state. | | | 2842 | 56.3 |
| | | | 3224 | 61.0 |
| Dull red heat. | | | 3230 | 64.6 |
| | | | " | 49.7 |
| | | | 2146 | 55.8 |
| Bright red heat. | | | 695 | 52.7 |
| | | | 728 | 40.1 |
| | | | " | 70.0 |
| | | | 592 | 78.5 |
| | | | 410.5 | 102.0 |
| | | | " | 59.3 |
| Dazzling red heat. | | | 362 | 75.7 |
| | | | 1124 | 94.6 |

(D=current in one direction ; R=current reversed.)

B= balance method ; S=slit method ; *r*=resistance in ohms.

The curves obtained by the slit method were not at all satisfactory, and the results given above for the principal emission are only approximate. They indicate, however, that the emission was complex.

Apparently the initial emission before the break is here

almost entirely K-emission. The readings obtained with the commutated direct current are near those given by the simple direct current regardless of its direction. The steadiness of conditions with the former was by no means all that could be desired, and this was probably one of the reasons for the exceedingly wide range of values obtained at the higher temperatures. There was at one place good evidence of the appearance of Na-emission ($m/H=23$). In order to make the calculated value of m/H change from around 40 to 80, assuming that the character of the emission remains the same, it would be necessary for d to be decreased by about 2.5 mm., which is extremely unlikely, even for a temperature difference of 1000° C. Besides, such a change could be observed without difficulty from outside the apparatus. At the highest temperatures the strip was easily seen on account of its luminosity, and no bending of the strip was noticed. Since with the present arrangement ions from different parts of the strip should undergo equal deflexions, the only explanation for these results seems to be that the emission at any temperature is composed of Mo^{+} ions, together with impurity emission consisting principally of K^{+} . The value of m/H obtained by the balance method varies with the proportion of impurities present. Inasmuch as the taking of these readings and the consequent heating were carried on continuously for a period of twenty-six hours, it is most probable that the impurity emission had been largely driven off by the end of the experiment, the permanent characteristic emission remaining.

After the experiment the distance d was measured and found to agree within .08 of 1 per cent. with the value determined at the outset.

The curves of increase of emission with decreasing resistance (rising temperature) resembled those of an ordinary thermionic current. The decay of the thermionic current with time is quite rapid, particularly at the start. This would of course point to the presence of an impurity emission. But as the emission has seemed to be largely due to impurities in most cases, it is impossible to say whether the emission which appears to be characteristic of MoS_2 suffers a decay or not. The experiments just described, and others made with direct current heating, indicate that this emission becomes more prominent after long heating, a fact which strengthens the conclusion that it is a characteristic emission.

As a means of further investigation, the method naturally suggests itself of heating the molybdenite on a platinum

strip, as in the experiments with salts. This was tried by placing some powdered MoS_2 at the centre of a Pt strip previously glowed out at about 1100°C . The following readings were obtained :—

| Remarks. | M. | R. | T. | m/H. |
|----------------------------------|----|-------|-------|-------|
| MoS ₂ on strip of Pt. | B | 9350 | 840° | 72·0 |
| | | 10000 | 755° | 41·9 |
| | | " | " | 41·7 |
| | | 10200 | 786° | 41·5 |
| | | 10500 | 833° | 42·35 |
| | | " | " | 41·15 |
| | | " | " | 41·1 |
| | | 10000 | 755° | 24·74 |
| | | " | " | 41·5 |
| New MoS ₂ inserted. | B | 850 | 520° | 39·36 |
| | | 870 | 552° | 32·04 |
| | | 869 | 552° | 38·68 |
| | | 900 | 600° | 74·4 |
| | | 690 | 695° | 48·5 |
| | | 726 | 772° | 40·35 |
| | | 740 | 802° | 40·8 |
| | | " | " | 89·65 |
| | | 745 | 811° | 39·82 |
| Fresh piece inserted. | B | 750 | 826° | 41·4 |
| | | 760 | 845° | 42·2 |
| | | 770 | 865° | 40·4 |
| | | 773 | 873° | 44·85 |
| | | 783 | 895° | 41·55 |
| | | 800 | 930° | 40·45 |
| | | 750 | 826° | 46·65 |
| | | 860 | 1060° | 40·8 |
| | | 863 | 1070° | 41·65 |
| | | 872 | 1090° | 40·25 |
| | | 884 | 1115° | 38·66 |
| | | 900 | 1150° | 46·9 |
| | | 920 | 1191° | 40·9 |

It is known that molybdenum combines with platinum at a high temperature, but no evidence that chemical action had taken place could be seen from the appearance of the strip after the experiment.

One notices that these values lie mainly around that for K-impurity emission. There is this departure, however : in all previous experiments when the K-emission was measured the values ranged, if anything, *lower* than the apparently

correct value, 39. Here the mean value is distinctly above this value. Furthermore, in no other case of heating a salt on a Pt strip have such high jumps in the values of m/H been experienced. Thus it may be possible that an emission of a heavy ion such as Mo^+ occurred, which most of the time was small compared to the K-emission, but which showed itself in spots where perhaps a fresh piece of MoS_2 had come into contact with the hot strip. No satisfaction could be obtained with the slit method, principally because the emission decayed so fast. Another feature of this experiment is the high temperature reached before emission was detected. This may be due simply to the small amount of the material heated as compared with the experiments with molybdenite strips.

In interpreting these results one notices the more or less constant presence of the familiar K^+ -emission, which for certainly a large part of the time renders indeterminate any other emission that may occur.

The next thing to strike the attention is the occasional high value of m/H , pointing to the emission of some heavy ion, the character of which is most probably a singly-charged atom of molybdenum. The average of these high values for m/H agrees with this conclusion, as it lies in the neighbourhood of 96. It does not seem possible that an emission of Mo^{++} ions was obtained, although if such an emission occurred its presence would be next to impossible to determine.

This characteristic emission usually attains a measurable value at the start of the break, about 310°C. , and may be detected anywhere beyond this point, depending upon the intensity of the accompanying impurity emission. It does not appear to be connected solely with one state or the other, or with the period of transition. More than this cannot be stated with any conviction.

9. Summary.

It appears from the foregoing experiments that no characteristic positive emissions are given off by the following salts:— AgCl , AgI , PbCl_2 , PbBr_2 , PtCl_2 , CuCl_2 . The same statement is probably true of AlF_3 . In the case of Cu_2Cl_2 there are indications of Cu^{++} . Thus the investigation has not shed much light on the question of the connexion between valency and the charges on the ions mentioned at the beginning of the paper. In nearly every case positive ions

have been found to be present for which the value of e/m corresponds to singly charged atoms, either of potassium or sodium, or of both these elements; so that the results confirm the conclusion previously reached by Richardson*.

It is possible that the characteristic emission from these salts occurs, but is too small for measurement with the apparatus used. It will be remembered that in many of the experiments a barely noticeable emission was detected at temperatures slightly below the melting point. If the apparatus could be made more delicate, it would be interesting to see whether or not this is the case.

Molybdenite has been found to possess a number of interesting electrical properties which include the following:—

(1) In the range of temperature between that of the room and a brilliant red heat this mineral exists in two distinct states.

(2) The resistance in the low voltage or low temperature state is very nearly an inverse exponential function of the absolute temperature.

(3) At ordinary room temperatures the resistance is a function of the applied potential difference and appears to approach the value infinity as the potential approaches the value zero.

(4) The conduction of electricity is evidently carried on mainly by electrons.

Two conclusions may be stated in regard to the thermionic emission from molybdenite.

I. A large emission from impurities,—principally the ordinary K^+ -emission.

II. A characteristic emission of Mo^+ ions, apparently having no exclusive relation to the break or to either state.

In conclusion, I wish to express my thanks to Prof. O. W. Richardson, who suggested the problem and under whose instruction the experiments were started, and to Prof. E. P. Adams for many helpful suggestions during the carrying on of the work. I am also indebted to Prof. Augustus Trowbridge for suggesting the test of molybdenite and for valuable advice during the trial of that substance.

Palmer Laboratory, Princeton, N.J.

April 26, 1916.

* Phil. Mag. vol. xxii. p. 669 (1911); Roy. Soc. Proc. A. vol. lxxxix. p. 507 (1914).

XXII. *A Note on Thermal Diffusion.* By S. CHAPMAN,
M.A., D.Sc., and F. W. DOOTSON, M.A., Sc.D.*

IN a recent memoir by one of us †, a new mathematical treatment of the kinetic theory of simple and composite gases is developed, in which it is shown that a temperature gradient in a mixture of two gases is sufficient to produce diffusion, independently of any non-uniformity of composition or of the action of external forces. This phenomenon, apparently first announced, has been designated "thermal diffusion." In the case of a uniform mixture of two gases, and in the absence of any other agent tending to produce diffusion, the effect of a temperature gradient maintained in the gas will be to make the heavier gas molecules diffuse in the direction of diminishing temperature, and *vice versa* for the lighter gas molecules. The amount of the effect is greatest when the gases are mixed in nearly equal proportions by volume, and also is greater the more unequal are the masses and diameters of the gas molecules. It depends, moreover, on the nature of the molecules; it seems greatest for molecules which behave like rigid elastic spheres, while it vanishes altogether in the one special case when they act like fifth-power centres of force (the model used by Maxwell in his later papers on the kinetic theory). The latter curious fact perhaps explains why the phenomenon remained undiscovered so long by theoretical writers, since till recently Maxwellian molecules were the only ones which could be treated with mathematical accuracy.

Let us suppose that a temperature gradient is maintained, by outside means, in a mixture of two gases occupying a closed vessel, there being no external forces. Thermal diffusion will act in the manner indicated, but there will be a limit to the inequality of composition thus set up, since such an inequality of composition tends to right itself by the ordinary process of diffusion. The amount of the resultant concentration-gradient, when the state of the gas has become steady, will depend on the ratio of the ordinary coefficient of diffusion, D_{12} (say), to a certain coefficient of thermal diffusion, D_t , which is defined in the memoir cited. This ratio, D_t/D_{12} , will be denoted by k_t . Let us denote the absolute temperature by T , and the proportions by volume of the heavier and lighter gas by v_1 and v_2 respectively (so that $v_1 + v_2 = 1$). Then, in the steady state, the concentration and

* Communicated by the Authors.

† Chapman, Phil. Trans. A. 1916 (unpublished); an abstract is given in Proc. Roy. Soc., December 1916.

temperature gradients at a point (x, y, z) are related to one another by three (x, y, z) equations of the form

$$\frac{\partial}{\partial x} \left(\frac{v_1}{v_1 + v_2} \right) = - \frac{\partial}{\partial x} \left(\frac{v_2}{v_1 + v_2} \right) = k_t \frac{\partial}{\partial x} (\log T). \quad (a)$$

Consequently it follows that, over a distance within which k_t may be regarded as constant, $v_1/(v_1 + v_2)$ varies as $k_t \log T$; since k_t is positive it is clear from this that the heavier gas should be relatively denser than the light, towards the cooler end of the vessel. The demonstration of this effect seems to afford the best method of verifying the theory, and our present object is to describe briefly some experiments undertaken with this end in view.

The experiments were made by the second author of this Note, and definitely establish the existence of the phenomenon of thermal diffusion. Pressure of other duties unfortunately rendered it impossible to perfect the apparatus so that it should be capable of yielding results of close numerical accuracy; the quantitative effect on the phenomenon, due to the various modifying factors mentioned above, was consequently not determined: thus, while the predicted sign and order of magnitude of the effect were both confirmed, the verification of the theory is to be regarded as mainly qualitative. Further experiments are now in progress at South Kensington, in which optical methods are being used for determining the composition of the gases before and after the action of thermal diffusion; by this means it is hoped to obtain observations of sufficient accuracy to enable the somewhat complex theory to be checked in all its more important features. The results of this second series of experiments will be published in due course.

The experiments of this paper fall into three groups. Those in the first group were made with a simple apparatus consisting of two glass bulbs of about 100 c.c. capacity, connected by a short tube provided with a stopcock of 5 mm. bore. This was sufficient to ensure equality of pressure in the two bulbs when opened, and to allow the diffusion process to proceed with fair rapidity. Due provision was, of course, made for the initial evacuation of the apparatus, the introduction of the gases to be experimented on, and for drawing these off to be analysed. The hot bulb was heated up to a temperature of about 230° C. by means of a small sand-bath. The gases used with this apparatus were carbon dioxide and hydrogen; they were chosen because of the ease with which they can be estimated, and because of their large mass-ratio (22).

A mixture containing nearly equal proportions of each, by volume, was introduced into the apparatus at atmospheric pressure; the outer connexions were closed, and with the intermediate stopcock open one bulb was heated up to 230°C ., the other being kept at the temperature of running water from the mains. The apparatus was left in this state for four hours, to allow some time for the thermal diffusion to take effect, and the stopcock was then closed. The proportion of CO_2 in the mixture contained in each bulb was then determined by analysis of samples drawn off (after cooling). The result was as follows:—

- (1) $\begin{cases} \text{Hot bulb } (230^{\circ}\text{C.}) & 44.9 \text{ per cent. } \text{H}_2 : 55.1 \text{ per cent. } \text{CO}_2. \\ \text{Cold bulb } (10^{\circ}\text{C.}) & 41.3 \text{ per cent. } \text{H}_2 : 58.7 \text{ per cent. } \text{CO}_2. \end{cases}$

Two further experiments on similar lines, but with rather different proportions of the two gases, were made, the time allowed being four hours in each case, as before; the results were as follows:—

- (2) $\begin{cases} \text{Hot bulb } (240^{\circ}\text{C.}) & 85.3 \text{ per cent. } \text{H}_2 : 14.8 \text{ per cent. } \text{CO}_2. \\ \text{Cold bulb } (10^{\circ}\text{C.}) & 83.4 \text{ per cent. } \text{H}_2 : 16.6 \text{ per cent. } \text{CO}_2. \end{cases}$
- (3) $\begin{cases} \text{Hot bulb } (200^{\circ}\text{C.}) & 53.2 \text{ per cent. } \text{H}_2 : 46.8 \text{ per cent. } \text{CO}_2. \\ \text{Cold bulb } (10^{\circ}\text{C.}) & 51.0 \text{ per cent. } \text{H}_2 : 49.0 \text{ per cent. } \text{CO}_2. \end{cases}$

An attempt was also made to perform a similar experiment using a mixture of sulphur dioxide and hydrogen, but it was unsuccessful at first: the hot bulb was raised to a low red heat, and the gases reacted to form sulphur and water. Later on, however, with a slightly different form of the apparatus, the phenomenon was clearly demonstrated also with these gases. In the new apparatus cylindrical tubes of wide bore took the place of the spherical bulbs, and the hot side was heated by an electric furnace formed of resistance-wires wound round a cylindrical tube of asbestos. The hot tube was of 200 c.c. capacity, and the cold one of half this size; they were joined by a tube of 10 mm. diameter, provided with a stopcock of 8 mm. diameter. In the first experiment with this apparatus the gases were analysed after only two hours, the result being as follows:—

- (4) $\begin{cases} \text{Hot bulb } (220^{\circ}\text{C.}) & 58.3 \text{ per cent. } \text{H}_2 : 41.7 \text{ per cent. } \text{SO}_2. \\ \text{Cold bulb } (10^{\circ}\text{C.}) & 57.9 \text{ per cent. } \text{H}_2 : 42.1 \text{ per cent. } \text{SO}_2. \end{cases}$

The differences hardly exceed the limits of experimental error, the time being insufficient for the attainment of the steady state: with this form of apparatus the diffusion

process would take place more slowly than with the previous one. In the next experiment, therefore, eighteen hours were allowed, and the results were

$$(5) \quad \begin{cases} \text{Hot bulb (220° C.)} & 63.2 \text{ per cent. H}_2 : 36.8 \text{ per cent. SO}_2. \\ \text{Cold bulb (10° C.)} & 59.7 \text{ per cent. H}_2 : 40.3 \text{ per cent. SO}_2. \end{cases}$$

Some experiments were also undertaken on a mixture of hydrogen and hydrochloric acid gas, but they were not continued since in every case there were indications that the acid had attacked the alkali of the glass.

The effect of thermal diffusion was verified qualitatively also in another way. The hot and cold bulbs were connected to the two sides of a tube (A) divided in the middle by a porous diaphragm. After the bulbs had been maintained at their respective temperatures sufficiently long for thermal diffusion to act, the stopcock between them was closed, and the gases were allowed to cool. The side taps connecting with A, which had till then been closed, were opened so as to admit the mixtures in the hot and cold bulbs to their respective portions of the tube A. The pressure was adjusted so as to be initially the same on the two sides of the diaphragm. The difference of composition of the mixtures on the two sides quickly manifested itself by the production of an inequality of pressure between them, owing to the more rapid diffusion and equalization of density of the lighter constituent of the mixture. A paraffin pressure-gauge showed differences of level amounting to 10 mm. or less, on the two sides, the gases used being hydrogen and carbon dioxide, and hydrogen and sulphur dioxide. In each case the sign of the difference indicated an initial excess of the lighter gas on the side of the hot bulb.

We will now briefly consider the theoretical difference of composition to be expected in the cases (1), (2), (3), and (5); in case (4) the steady state would appear not to have been attained, so that we may neglect the figures for that experiment. We will write

$$\begin{aligned} \lambda_1 &= v_1/(v_1 + v_2), & \lambda_2 &= v_2/(v_1 + v_2), \\ \lambda_{12} &= \lambda_1/\lambda_2, & \lambda_{21} &= \lambda_2/\lambda_1. \end{aligned}$$

The equation (a) may be conveniently re-written as follows:—

$$\frac{\partial \lambda_1}{\partial x} = - \frac{\partial \lambda_2}{\partial x} = k_t \frac{\partial \log T}{\partial x}.$$

It is easy to calculate a first approximation to k_t on the

assumption that the gas molecules behave like rigid elastic spheres. Using the formulæ in the Abstract already cited, the following expressions for k_t are obtained* :—

$$\text{Hydrogen and carbon dioxide, } k_t = \frac{33 \cdot 1\lambda_1 + 5 \cdot 42\lambda_2}{47 \cdot 2 + 86 \cdot 5\lambda_{12} + 5 \cdot 58\lambda_{21}}.$$

$$\text{Hydrogen and sulphur dioxide, } k_t = \frac{67 \cdot 3\lambda_1 + 5 \cdot 60\lambda_2}{65 \cdot 7 + 168\lambda_1 + 4 \cdot 4\lambda_2}.$$

The values of k_t corresponding to experiments (1), (2), (3), and (5) respectively are consequently approximately equal to

$$0 \cdot 138, \quad 0 \cdot 101, \quad 0 \cdot 138, \quad \text{and} \quad 0 \cdot 165.$$

The corresponding values of $\log_e T_1/T_2$, where T_1 and T_2 are the absolute temperatures of the hot and cold bulbs, are respectively

$$0 \cdot 56, \quad 0 \cdot 595, \quad 0 \cdot 515, \quad \text{and} \quad 0 \cdot 554.$$

The percentage differences of composition between the two bulbs, calculated from the approximate formula $100k_t \log_e T_1/T_2$, are as follows :—

$$7 \cdot 7, \quad 6 \cdot 0, \quad 7 \cdot 1, \quad \text{and} \quad 9 \cdot 1.$$

These correspond to the observed values

$$3 \cdot 6, \quad 1 \cdot 8, \quad 2 \cdot 8, \quad \text{and} \quad 3 \cdot 5.$$

The signs of the observed differences are correct in every case, but the magnitudes of the differences are not equal to the theoretical values just given. The experimental results are, of course, not exact, and there is perhaps room for doubt (except in case 5) as to whether the steady state, corresponding to the maximum difference of composition, was in all cases attained. The excess of the calculated over the observed differences, however, is easily explicable as arising from the fact that the molecular model chosen as the basis of the calculations is that for which k_t has its maximum value, while it is not the model which most closely represents actual gas molecules. The effect of this can be sufficiently illustrated, without going into any very detailed analysis, by the example of a gas in which the molecules of one kind are very small

* The values assumed for the radii of the molecules of H_2 , CO_2 , and SO_2 respectively were 1.18, 1.64, and 2.00, the unit being 10^{-8} cm. The two former values are those given on p. 476, Phil. Trans. A. cxi.; the last is assumed, as we do not know of any reliable determination of the radius of the SO_2 molecule.

in size and mass compared with those of the other kind. In this case it is easy to calculate first approximations to k_t for molecules which behave like centres of forces proportional to the inverse n th power of the mutual distance. The results for a few typical values of n are:—

$$n = 5, \quad 7, \quad 9, \quad 13, \quad 17, \quad 33, \quad \infty.$$

$$k_t = 0, \quad 0.156, \quad 0.227, \quad 0.294, \quad 0.326, \quad 0.372, \quad 0.417.$$

The last case also corresponds to rigid elastic spherical molecules. Now the values of n which give the best representation of actual gas molecules are found, from the investigation of the variation of viscosity with temperature, to range from 5 to 12 (*cf.* Jeans's 'Dynamical Theory of Gases,' p. 302, 2nd edit.). In the case of such a gas mixture as we are now considering, therefore, the value of k_t is likely to be less than one half the value calculated on the hypothesis of rigid elastic spherical molecules: and although, in the case of the gases to which our experiments relate, the mass-ratio and size-ratio are not such that the above calculations apply strictly to them, the general character of the result is likely to be the same. The calculated values of k_t (0.138 and so on) are slightly too small for rigid spherical molecules (since further approximations would increase them by a few per cent.), but they are probably twice or thrice too large for actual gas molecules; and when this is allowed for, the experimental confirmation of the theory, within the limits of the experiments, appears to be as satisfactory as could be desired.

Cambridge, December 1916.

XXIII. *High Vacuum-Spectra of Gases.* By Prof. D. N. MALLIK, *D.Sc., F.R.S.E.,* and Prof. A. B. DAS, *M.Sc.**

[Plate IV.]

1. **W**HEN an electric discharge is passed through a vacuum-tube it seems to be reasonable to argue, *a priori*, that there would be a change in the character of the spectrum at very high vacua. For in a discharge-tube, when the contained gas is at moderately high pressure, there are mutual collisions of corpuscles, positive particles, atoms, and molecules, so that the modes of motion of a luminous gas-particle in such a tube must be many—though limited by the

* Communicated by the Authors. Paper read before the Third All-India Science Congress, 1916.

strained condition imposed by the nature of the gas. Hence the spectrum must be complex under these circumstances.

At a very low pressure, however, on account of the simpler conditions that prevail, the modes of motion must be fewer, and the corresponding spectrum also simpler in consequence.

2. Under these circumstances also an application of a magnetic field is more likely to result in an effect being produced than under ordinary conditions. Moreover, if a vortical spin is associated with the structure of an atom and each period of a spin corresponds to a line in the spectrum, a change in the spin, conceivably produced by an impressed magnetic field, and a corresponding change in period must lead to a displacement of the lines.

It will follow also that the gas ought to show a simplified spectrum, which may be the same for all gases.

Experiments, so far as they have gone, tend to confirm these conclusions.

3. When photographs of spectra of air are taken at different pressures, it is found (Pl. IV. fig. I., spectra of air for pressures between 33 to 3 mm.) that there is no change up to a pressure of $\frac{1}{100}$ of millimetre in a tube of length 14.5 cm. with an induction-coil giving a spark-length of 29 mm. in atmospheric air.

4. At a pressure of about $\frac{1}{100}$ millimetre, however, the character of the spectrum seems suddenly to change, giving a partially simplified spectrum (Pl. IV. fig. II., spectra 2, 4), while a simple spectrum of four lines, consisting of four of the original lines, is obtained when the pressure is about $\frac{1}{1000}$ of a millimetre (Pl. IV. fig. v., spectrum 3). Figs. III. and IV. represent intermediate stages.

On introducing the magnetic field there seems to be a small shift, which, however, requires further examination (Pl. IV. fig. v., spectra 1, with the magnetic field on, 2, with the field reserved, 3, without the field).

5. If this shift is not fortuitous, it ought to prove of great theoretic interest. Larmor has shown that on his (or any other) dynamical theory of the electromagnetic field, an effect ought to be observable in a strong magnetic field, which, however, Lodge failed to detect.

It may be observed that if any such effect is to be observed it is more likely to be detected under the simpler conditions that obtain in high vacua than in those in Lodge's experiments.

6. It will be noticed that at a certain low pressure the magnetic field produces increased illumination (Pl. IV. figs. IV., v.). When a simplification of spectrum occurs at a

higher pressure than this, the effect of the magnetic field is to restore the original spectrum (Pl. IV. fig. II., spectra 1, 3).

The explanation of the increased illumination and restoration of the original spectrum seems to be that the magnetic field forces more ions through the gas—from one electrode to the other,—which were previously proceeding direct to the sides of the vessel, and the consequent increase in ionization and in the number of collisions will naturally produce increased illumination as well as restore the conditions for a complex spectrum, as compared with those that obtained before the application of the magnetic field.

7. Experiments with hydrogen, so far as they have gone, seem to give similar results. It should be noted, however, that, as is well known, spectra of hydrogen generally present features which are difficult to analyse. The results for hydrogen, therefore, have to be tested by further experiments before we can be sure of their accuracy. We accordingly withhold the detailed results for hydrogen till these are duly tested.

8. Various investigators have studied the spectra of electric discharge through gases. These researches relate mostly, however, to discharge under high pressure. Thus, according to W. J. Humphreys, an increase of pressure causes all isolated lines to shift towards the red end of the spectrum, but the lines of bands are not apparently shifted. Also, different series of lines of a given element are displaced to different extents, but similar lines of an element, though not belonging to any recognized series, are displaced equally, the pressure-shifts of similar elements being periodic functions of the atomic weights. In a later paper he suggested that there might be a direct connexion between the pressure-shift and the Zeeman effect; but R. Rossi, who employed pressures of 15, 30, 50, and even 100 atmospheres, failed to detect any relation between them.

9. Influence of pressure upon absorption spectra has been studied by A. Dufour and others, while in the case of arc-spectra W. G. Duffield has shown that increase of pressure from 1 to 201 atmospheres broadens all silver lines, and J. Barnes has noticed an increase in the intensity of the spark lines of Al and Mg, and a diminution in the number of arc lines of Cu under reduced pressure. Reference should also be made in this connexion to the single-line spectra of metals Hg, Zn, Cd, studied by Frank and Hertz and McLennan and Henderson. They have shown that when heated vapour of these elements is traversed by electrons

possessing kinetic energy above a certain limiting value, they emit a single-line spectrum of determinate wave-length.

10. It is interesting to note that low-pressure effects on spectra have not engaged the attention of physicists to the same extent. Considerable attention has, however, been devoted in recent years to the investigation of the spectra of metals *in vacuo*.

11. Coming, finally, to the case of discharge in vacuum-tubes, reference should be made to the work of R. W. Lawson, who found that variation of the current density and voltage in the discharge-tube did not produce any change in the relative intensity of the nitrogen bands, but considerable difference resulted from pressure changes. In the case of air, oxygen lines were not discernible, the spectrum being the same as that of nitrogen. It appears, accordingly, that no previous worker has (so far as we have been able to discover) noticed the simplification of the spectrum of air in a discharge-tube with which the present paper deals.

Our thanks are due to the authorities of the Presidency College for offering us facilities for carrying on these researches in the Presidency College Laboratory, Calcutta.

XXIV. *On Maxwell's Stresses*. By MEGH NAD SHAHA, *M.Sc., Research Scholar in Mathematical Physics, Sir T. N. Palit College of Science, Calcutta* *.

1. MAXWELL † has shown that the mechanical action between two electrical systems at rest can be accounted for by assuming the existence of certain stresses distributed over a surface completely enclosing one of the systems. If ψ be the potential at any point due to the whole system, the X-component of the mechanical force on one of the systems can be shown to be

$$F_x = \frac{1}{4\pi} \iiint \frac{\partial \psi}{\partial x} \nabla^2 \psi \, dx \, dy \, dz, \quad . \quad . \quad . \quad (1)$$

where the integration extends over the space occupied by the first system.

2. If the force is really due to the presence of stresses on a surface enclosing the first system, we have

$$F_x = \iint X_x \, dS = \iint (\ell X_x + m X_y + n X_z) \, dS, \quad . \quad . \quad (2)$$

where X_x , X_y , X_z &c. . . . are the various surface-tractions,

* Communicated by Prof. D. N. Mallik.

† Maxwell, 'Electricity and Magnetism,' vol. i. chap. v.

and (l, m, n) are the direction cosines of the normal to the surface.

By transforming expression (2), we obtain

$$F_x = \iiint \left(\frac{\partial X_x}{\partial x} + \frac{\partial X_y}{\partial y} + \frac{\partial X_z}{\partial z} \right) dx dy dz.$$

$$\begin{aligned} \text{Since } \frac{1}{4\pi} \frac{\partial \psi}{\partial x} \nabla^2 \psi &= \frac{\partial}{\partial x} \left[\frac{1}{8\pi} \left\{ \left(\frac{\partial \psi}{\partial x} \right)^2 - \left(\frac{\partial \psi}{\partial y} \right)^2 - \left(\frac{\partial \psi}{\partial z} \right)^2 \right\} \right] \\ &+ \frac{\partial}{\partial y} \left[\frac{1}{4\pi} \frac{\partial \psi}{\partial x} \cdot \frac{\partial \psi}{\partial y} \right] \\ &+ \frac{\partial}{\partial z} \left[\frac{1}{4\pi} \frac{\partial \psi}{\partial x} \cdot \frac{\partial \psi}{\partial z} \right], \end{aligned}$$

we have, putting $\frac{\partial \psi}{\partial x} = X$, $\frac{\partial \psi}{\partial y} = Y$, $\frac{\partial \psi}{\partial z} = Z$,

$$\begin{aligned} \iiint \left\{ \frac{\partial}{\partial x} \left[X_x - \frac{1}{8\pi} (X^2 - Y^2 - Z^2) \right] + \frac{\partial}{\partial y} \left[X_y - \frac{1}{4\pi} XY \right] \right. \\ \left. + \frac{\partial}{\partial z} \left[X_z - \frac{1}{4\pi} XZ \right] \right\} dx dy dz = 0. \quad (3) \end{aligned}$$

Maxwell concludes from this that a system of stresses

$$\begin{aligned} X_x &= \frac{1}{8\pi} (X^2 - Y^2 - Z^2), & Y_y &= \frac{1}{8\pi} (Y^2 - Z^2 - X^2), \\ Z_z &= \frac{1}{8\pi} (Z^2 - X^2 - Y^2), & X_y &= \frac{1}{4\pi} XY, & Y_z &= \frac{1}{4\pi} YZ, \\ & & Z_x &= \frac{1}{4\pi} ZX, & & \dots \dots \dots (4) \end{aligned}$$

distributed over the surface S account for the mechanical action quite satisfactorily, and therefore provide a concrete physical representation of the mechanism of electrostatic action.

3. But the expressions (4) are not complete solutions of the integral equation (3). Maxwell* himself points out that they can at best be regarded as a first step towards the solution of equation (3). Many investigators, including Sir J. J. Thomson†, have pointed out that æther cannot possibly be at rest under these stresses. Lorentz‡ goes so far as to say that the stresses are simply mathematical fictions, which can be conveniently utilized for the calculation of radiation pressure and other allied phenomena. The object

* *Loc. cit.* p. 165 *et seq.*

† *Loc. cit.* p. 165, footnote.

‡ 'Theory of Electrons,' p. 31.

of the present paper is to show that the stresses cannot account for the energy of electrification, if the medium is to be regarded as an elastic solid.

4. The energy of a charged system can be expressed as a volume integral,

$$W = \frac{1}{8\pi} \iiint \left[\left(\frac{\partial \psi}{\partial x} \right)^2 + \left(\frac{\partial \psi}{\partial y} \right)^2 + \left(\frac{\partial \psi}{\partial z} \right)^2 \right] dx dy dz. \quad (5)$$

Maxwell* states that the quantity W may be interpreted as the energy in the medium due to the distribution of stresses; but the statement is not proved. The only rational meaning which we can attach to this assertion is that the energy of electrification arises from the elastic displacement of æther particles. I am not aware whether any other interpretation has been or can be given to Maxwell's statement, but it has generally been taken in this sense, though Maxwell himself is rather vague on the point. We should naturally expect that energy calculated on this understanding would lead to the expression (5), but that this is not the case will be presently shown.

5. If u, v, w be the elastic displacements of a particle of the dielectric medium, the energy of deformation or the train-energy function is

$$W' = \iiint_{\text{initial state}}^{\text{final state}} \rho (X\delta u + Y\delta v + Z\delta w) dx dy dz \\ + \iiint_{\text{initial state}}^{\text{final state}} (X_v\delta u + Y_v\delta v + Z_v\delta w) dS, \quad (6')$$

and this can be shown to be equivalent to

$$\frac{1}{2} \iiint (X_x e_{xx} + Y_y e_{yy} + Z_z e_{zz} + X_y e_{xy} + Y_z e_{yz} + Z_x e_{zx}) dx dy dz.$$

Assuming the æther to be isotropic and to behave as an elastic solid, we can put

$$\begin{bmatrix} e_{xx} \\ e_{yy} \\ e_{zz} \end{bmatrix} = \frac{1}{E} \begin{bmatrix} 1 & -\sigma & -\sigma \\ -\sigma & 1 & -\sigma \\ -\sigma & -\sigma & 1 \end{bmatrix} \begin{bmatrix} X_x \\ Y_y \\ Z_z \end{bmatrix},$$

and
$$e_{xy} = \frac{X_y}{\mu}, \quad e_{yz} = \frac{Y_z}{\mu}, \quad e_{zx} = \frac{Z_x}{\mu}.$$

* 'Electricity and Magnetism,' p. 165.

Then, after some calculation, the strain-energy function comes out to be

$$W' = \frac{1}{2} \frac{3(1+2\sigma)}{\epsilon(1+\sigma)} \iiint \left(\frac{R^2}{8\pi^2} \right)^2 dx dy dz. \quad . \quad . \quad (6)$$

It will thus be seen that if the stresses are really existent, and if they are amenable to the ordinary laws of elasticity, the strain-energy function, or the energy of elastic deformation of the medium, is $\frac{3}{2} \frac{(1+2\sigma)}{\epsilon(1+\sigma)} \left(\frac{R^2}{8\pi^2} \right)^2$ per unit volume. But this is very different from the theorem that the energy density per unit volume is $\left(\frac{R^2}{8\pi} \right)$, which is derived from electrostatic principles.

6. Since nothing definite is known about the elastic constants of æther, we cannot draw any conclusion from (6) about the energy distribution in æther. Maxwell's stresses are thus seen to fail to account for the energy of electrification, on the understanding that the medium behaves like an elastic solid.

7. It is well known that the energy-distribution theorem is proved on the basis of the empirical laws of electrostatics. No use is made of the stresses. The result is purely analytical, and says that if energy is distributed all over space as a continuous function with volume density $\frac{R^2}{8\pi}$, the total energy will come out to be the same as the total energy of electrification. The distinction between Maxwell's view of energy distribution as due to stresses (in the sense we have interpreted it) and the actual case can be better brought out if we adopt the following modified method of proving the energy-distribution theorem. Suppose we have an electrical system consisting of charged surfaces, and particles in a given configuration. The energy of electrification will be the same in whichever way we may bring about the final configuration. Suppose that, to start with, the charges and the charged surfaces were all at an infinite distance, and the given configuration is brought about by properly moving the charged surfaces and other discreet electrified particles. Then the energy of electrification is

$$\begin{aligned} W &= \sum \int e \delta V, \\ &= \sum \iint \sigma \left(\frac{\partial V}{\partial x} \delta x + \frac{\partial V}{\partial y} \delta y + \frac{\partial V}{\partial z} \delta z \right) dS, \\ &+ \sum \iiint \rho \left(\frac{\partial V}{\partial x} \delta x + \frac{\partial V}{\partial y} \delta y + \frac{\partial V}{\partial z} \delta z \right) dx dy dz, \end{aligned}$$

where σ is the surface density of electricity on a charged surface, and ρ is the volume density. Since $\frac{\partial V}{\partial x}$ is the x -component of electrical force on a surface, $\sigma \frac{\partial V}{\partial x}$ is the x -component of mechanical action per unit surface. Similarly, $\rho \frac{\partial V}{\partial x}$ is the x -component of mechanical force per unit volume of electrified particles. We can therefore put

$$W = \Sigma \iint (X_v \delta x + Y_v \delta y + Z_v \delta z) + \Sigma \iiint (X \delta x + Y \delta y + Z \delta z).$$

8. Comparing this expression for energy with the expression (6)

$$W' = \iint (X_v \delta u + Y_v \delta v + Z_v \delta w) + \iiint \rho (X \delta u + Y \delta v + Z \delta w), \quad (6)$$

we see that in the present case (X_v , Y_v , Z_v) are the components of surface-tractions on a charged surface, and (X , Y , Z) are the body-forces on electrified particles. The existence of these forces can be experimentally demonstrated, and they exist only in regions occupied by electricity; elsewhere they are nil. The energy of electrification is derived from the work done in the actual displacements (δx , δy , δz) of these charged regions towards each other. On the other hand, (X_v , Y_v , Z_v) in (6) are the tractions on a surface enclosing some of the charged regions, and δu , δv , δw are their elastic displacements. We may by special assumption identify the two systems of surface-tractions and body-forces, but the actual displacements (δx , δy , δz) and the elastic displacements (δu , δv , δw) cannot be identified in any way. The two expressions represent fundamentally different quantities.

9. The fact that radiant energy would exert a definite amount of pressure on material surfaces was first predicted by Maxwell on the hypothesis of dielectric stresses. Now that radiation pressure is an experimental fact, it has been supposed by some physicists that Maxwell's stresses must have a material existence. But it is well known that radiant energy can be deduced independently of the stresses. Bartoli has shown that the pressure of radiant energy can be deduced from thermodynamic principles. Planck* has deduced it from electrodynamical principles, assuming that the perfect reflector is a super-conductor of electricity. This

* Planck, *Wärmestrahlung*, second edition, pp. 49 *et seq.*

is an ideal limiting case of the experimental fact that good conductors of electricity are also good reflectors of radiant energy. The electric vector accompanying a ray of light gives rise to a finite charge on the surface of the superconductor and a finite current within the conductor. The charge exerts a negative pressure on the surface, while the current, in presence of the field of the magnetic vector accompanying the ray, produces a mechanical force in the contrary direction. The resultant of the two, when averaged statistically, yields the radiation pressure. How far these theories are consistent with the theory of stresses may form a subject for interesting investigations.

My best thanks are due to Prof. D. N. Mallik for his kind help and encouragement.

XXV. *Notes on Osmotic Theory.*
By the Earl of BERKELEY, F.R.S.*

ONE of the chief difficulties in understanding osmotic theory seems to lie in the unavoidable complexity of the notation. This complexity arises from the fact that there are two sets of osmotic pressures, depending on which component is regarded as the solvent, and each of these sets is again capable of differentiation into another two sets according as the pressure on the solution or the pressure on the solvent is to be regarded as constant. Again, from the definition of osmotic pressure—namely, that it is the difference between the pressure on the mixture and that on the pure component when the two are in equilibrium through a semi-permeable membrane,—it is easy to see that, replacing the solution by a mixture of vapours and the pure solvent by pure vapour, there will be yet another eight sets of osmotic pressures. We can even extend the definition to cover the case of any liquid (or solution) which, when under pressure, is in equilibrium through a membrane with its own vapour under a different pressure.

In fig. 1 all but two of the possible states of osmotic equilibrium are shown †.

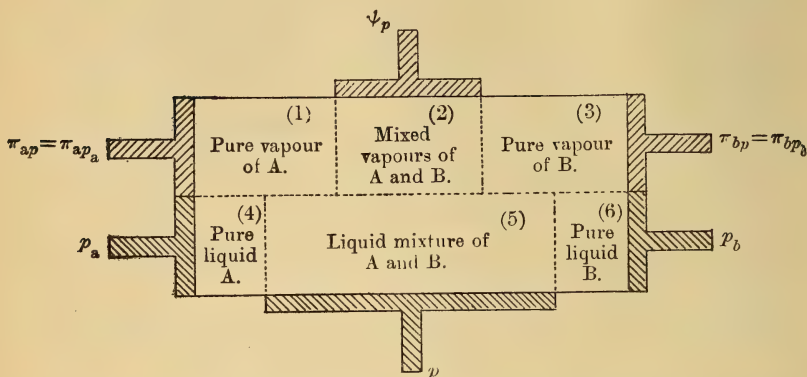
The dotted lines represent semi-permeable membranes; the left-hand membranes are permeable to component A only and the right to B only. The left-hand half of the horizontal membrane separating compartment (2) from (5)

* Communicated by the Author.

† The two that are omitted are those between compartment (2)/(4) and (2)/(6).

is supposed to be permeable to the vapour of A, whilst the right-hand half is permeable to that of B.

Fig. 1.



Bearing all these possibilities in mind, it is obvious that some systematic scheme of notation is required. The following, which has been worked out in conjunction with Mr. G. W. Walker, seems to provide for most of the possible combinations. In elaborating the scheme we have kept three desiderata before us:—

- (1) The number of separate symbols should be few, so as to lessen the burden on the memory.
- (2) The symbols which have already acquired, so to speak, a prescriptive right are retained as far as possible.
- (3) The notation should be simple, so* that the symbols and their suffixes are, as near as may be, self-explanatory.

THE NOTATION.

All Latin letters refer to liquids, whilst Greek letters are reserved for vapour or gases (this does not apply to the suffixes), and the corresponding letters of the two alphabets (except in the case of p and ψ) denote corresponding quantities.

For the Solution and Mixed Vapours.

p and ψ^* are the pressures on the solution and mixed vapours respectively.

* For the sake of symmetry, π (without a suffix) would have been the right letter, but it has been found in practice that the use of π here is inconvenient.

z and ζ are the specific volumes of the solution and mixed vapours respectively.

s_a and σ_a are the apparent spec. vols.* of component A in the solution and mixed vapours respectively.

s_b and σ_b are the apparent spec. vols. of component B in the solution and mixed vapours respectively.

a and α are the number of grammes of A per gramme of solution and mixed vapours respectively.

b and β † are the number of grammes of B per gramme of solution and mixed vapours respectively.

Note that $a + b = \alpha + \beta = 1$.

For the pure Components, Liquid or Vapour.

p_a and π_a are the pressures on the pure liquid A and on the pure vapour of A respectively.

p_b and π_b are the pressures on the pure liquid B and on the pure vapour of B respectively.

z_a and ζ_a are the specific volumes of pure liquid A and pure vapour respectively.

z_b and ζ_b are the specific volumes of pure liquid B and pure vapour respectively.

When it is necessary to specify that the quantities are those belonging to vapour in equilibrium with a liquid under a particular pressure, that pressure will, following Porter's notation (Proc. R. S., A. vol. lxxix. 1907, p. 519), be denoted by adding it as a suffix. Thus :

ψ_p is the pressure on the mixed vapours when they are in equilibrium with the solution under pressure p .

π_{ap} is the pressure on the pure vapour of component A when it is in equilibrium with the solution (of concentration a) under pressure p ; and with the mixed vapours (of concentration α) when the pressure on them is ψ_p .

* The term "apparent specific volume" is used for brevity's sake ; the quantities referred to represent the change in volume of a large mass of solution (or mixed vapours) when one gramme of the component under discussion escapes from it under (osmotic) equilibrium conditions. That is to say, we assume that the mass of the solution is so large that, after this operation, there is no first-order change either in the osmotic pressure or in the concentration. The relation between the true and apparent specific volumes of any component in a solution is discussed in a communication to the Royal Society, entitled "Osmotic Pressures derived from Vapour-pressure Measurements."

† It is to be noted that the concentration of the components in the mixed vapour is by no means always the same as in the liquid mixture.

ψ_ψ is the pressure on the mixed vapours when they are in equilibrium (*through a membrane*) with the solution under the same pressure *.

$\pi_{a\pi}$ is the pressure of the pure vapour of component A when it is in equilibrium (*through a membrane*) with the pure liquid A under the same pressure *.

ψ_0 and π_{a0} will be reserved to denote the values of ψ_ψ and $\pi_{a\pi}$ when no membranes are present.

π_a is the partial pressure of component A in the mixed vapours.

π_β is the partial pressure of component B in the mixed vapours.

The Osmotic Pressures.

P_a and P_b are those of the solution when the membrane is permeable to liquid A or B respectively. They will be referred to as complementary osmotic pressures.

$$P_a = p - p_a \text{ and } P_b = p - p_b.$$

Π_a and Π_β are those of the mixed vapours (measured against a pure vapour) when the membrane is permeable to the vapour of A or B respectively.

$$\Pi_a = \psi - \pi_a \text{ and } \Pi_\beta = \psi - \pi_\beta.$$

$P_{a\beta}$ is that of the solution when the membrane is permeable to the vapours of both A and B.

P_a and P_β are those of the solution in contact with the mixed vapours when the membrane is permeable only to the vapour of A or B respectively.

$$P_{a\beta} = P_a = P_\beta = p - \psi_p.$$

That these three osmotic pressures are equal will be seen later. In practice it is convenient to distinguish between them.

P_a and P_b are those of the solution in contact with the pure vapours when the membrane is permeable to the vapour of A or B respectively.

$$P_a = p - \pi_a \text{ and } P_b = p - \pi_b.$$

* It is to be remarked that neither ψ_ψ nor $\pi_{a\pi}$ is uniquely defined, for, with a membrane present, it is possible to have a series of values of (say) π_a which will satisfy the definition.

P_{aa} and P_{bb} are those of the pure liquids in contact with their pure vapours respectively.

$$P_{aa} = p_a - \pi_a \quad \text{and} \quad P_{bb} = p_b - \pi_b.$$

$P_{a\alpha}$ and $P_{b\beta}$ are those of the pure liquids in contact with the mixed vapours through a membrane permeable to the vapour of A or B respectively.

$$P_{a\alpha} = p - \psi \quad \text{and} \quad P_{b\beta} = p - \psi.$$

It will be noticed that throughout this notation the suffixes a , b , α , and β indicate, as far as possible, which membranes are supposed to be operative; and they also specify the concentrations of the mixture, whether liquid or vapour. In working with the notation it will be found that this double use of the suffix leads to no ambiguity; indeed, it helps very materially in forming a mental picture of the various operations.

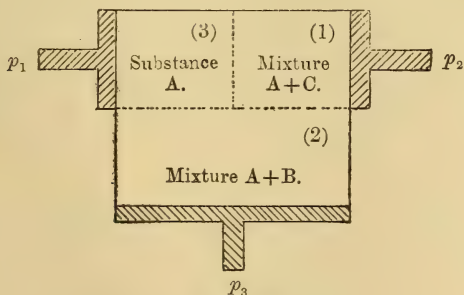
THEORY.

The Equivalence Theorem.—I will, in the subsequent pages, use this locution to denote the following theorem. "If we have any sets of molecules A, B, C, etc., each in osmotic equilibrium with a set X, then the original sets are in osmotic equilibrium with one another."

Before proving this for any state of matter (it is generally accepted for solutions), we must postulate that, in general, the osmotic pressure of any mixture increases with increase of concentration; should it diminish, instability would set in.

Now consider the system shown in fig. 2, where the dotted lines are membranes permeable to A only. Under the

Fig. 2.



pressures indicated, (1)/(3) and (2)/(3) are postulated to be in osmotic equilibrium. It is required to prove that (1)/(2) are also in equilibrium.

Assume that they are not, and let the defect be in the direction that more of substance A passes from (2) to (1) so that (1) becomes more dilute; but (1) and (3) were originally in equilibrium, and to restore this some A must pass through into (3). On the other hand, the mixture in (2) has been concentrated. Hence some of A will be required to pass from (3) to (2), and perpetual motion results. Now, in all these operations definite changes in volume are taking place (this follows from our definition of s_a and σ_a), so that the system could be harnessed to do external work, and consequently the motion is impossible. A similar result follows if we assume the defect in equilibrium to be in the opposite direction, and that a flow of substance A takes place from (1) to (2).

Applying the equivalence theorem to the system in fig. 1, it is easy to see that it is in equilibrium. For, taking compartments (1), (4), and (5), the solution is supposed to be in osmotic equilibrium with the pure liquid in (4), and the latter with its vapour in (1), so that (1) and (5) are in equilibrium*. But the pressure π_p can be adjusted so that the mixed vapours are in equilibrium with the solution; hence (1) and (2) are in equilibrium, similarly for (5), (6), and (3), and, therefore, for (5), (2), and (3).

In the foregoing notation the two components have been regarded as miscible in all proportions. This seems to be the most general case for osmotic pressures, but special cases can be dealt with under the same notation.

Thus, suppose the two components are miscible only over restricted ranges of concentrations, and that we are dealing with a solution and its conjugate; if so, we have the most complicated sets of equilibria possible for binary mixtures. The notation can be extended at once to cover such a case by assigning dashes to the suffixes a and b to represent the conjugate. It should be noted that α and β need not be altered, for both solutions have the same vapour-pressures (and osmotic pressures). Other special cases, such as solutions of non-volatile components whether solid or liquid, are obviously easily dealt with.

* Incidentally, this affords a simple proof that $\pi_{ap} = \pi_{ap_a}$ or $\pi_{a0} = \pi_a \pi$. Further, if we keep p_a constant and change the concentration in (5), the method will show that the change in p necessary to retain osmotic equilibrium will always be such that the vapour-pressure of the solution remains constant and equal to that of the solvent.

A general Method for connecting the several Osmotic Pressures with the Physical Properties of the Fluids under consideration.

Before proceeding to the discussion of the osmotic pressures, it will be necessary to establish three propositions :—

(a) When a solution is in osmotic equilibrium with its mixed vapour through a membrane permeable to both components, the closing of the membrane to one of the components alters neither the equilibrium nor the concentrations.

Consider compartments (1), (2), (5) of fig. 1; these are already in osmotic equilibrium. Let the right-hand half of the horizontal membrane between (2) and (5) (permeable to B) be closed. It is easy to show by the equivalence theorem that no disturbance takes place. Again, consider compartments (2), (3), and (5), and close the left-hand half—the equivalence theorem proves similarly that no disturbance results.

(b) It is possible to change the pressures on the solution and its mixed vapours (separated from one another by a membrane permeable to both components) in such a manner as to keep osmotic equilibrium between them without any change in concentration taking place.

For consider compartments (1), (2), and (5) :—Close the membranes between (2) and (5), and alter the pressures on (1) and (2) from ψ_p to $\psi_{p'}$ and π_{ap} to $\pi_{ap'}$ in such a way as to keep osmotic equilibrium through the membrane (1)/(2), and, at the same time, alter the pressure on the solution to p' so as to keep it in equilibrium with (1) through the membrane (1)/(5); then, on opening the membrane (2)/(5), if we apply the equivalence theorem, it can be shown that compartments (2) and (5) are still in equilibrium. Now, as (2) and (5) were in equilibrium to begin with, and are so at the end, we can state that the pressures on these two compartments could have been altered progressively and simultaneously without any disturbance of the osmotic equilibrium through the membrane.

(c) It is possible to change the pressures on the solution and its mixed vapours, separated from one another by a membrane permeable to either component only, in such a manner as to keep osmotic equilibrium between them without any change in concentration taking place.

This proposition is at once self-evident, if we remember that, at any stage in the alterations of the corresponding

pressures on solution and mixed vapours, we can close either half of the membrane and apply proposition (a).

It can be deduced easily from proposition (b) that one concentration of mixed vapours *only* can be in osmotic equilibrium with the solution through the *double* membrane; in other words, given a solution of definite concentration, the mixed vapour in osmotic equilibrium with it through a membrane permeable to both components can have one concentration and one only, and this concentration is independent of the equilibrating pressures.

Moreover, it is clear that mixed vapours in all possible relative concentrations can also be in equilibrium with the solution (and also with its mixed vapour) through a membrane permeable to *one* component only, provided the correct pressures be put upon them.

We can now proceed to the general method.

Consider compartments (1), (2), (4), and (5) of fig. 1. Over a large range of pressures any two of these can be in osmotic equilibrium through a membrane permeable to substance A; we can therefore, in general, perform an isothermal reversible cycle between two compartments.

Take compartments (1) and (2) as an example (in all the cycles the two compartments under consideration are supposed to be shuttered off from the remainder of the system). Let the pressure in (1) be π_a when in equilibrium with (2) under pressure ψ , and let them also be in equilibrium at some other two pressures π_a' and ψ' ; then, pass one gramme of substance A through the membrane from (1) to (2) under the original pressures, and then change the pressures to π_a' and ψ' (in such a manner that none of A passes through the membrane); then return the one gramme from (2) to (1) and restore the original pressures. The application of the laws of thermodynamics shows that $\int p dv$ taken round the cycle is zero; hence it follows at once that

$$\int_{\pi_a}^{\pi_a'} \zeta_a dp = \int_{\psi}^{\psi'} \sigma_a dp. \quad . \quad . \quad . \quad . \quad (1)$$

Carrying out similar cycles for the other pairs of compartments, six equations will result, as there are four compartments which can be taken two at a time. These six equations, if appropriate values for the limits be imposed, can be combined so as to connect any three or all four of the compartments.

In the same way we can get another set of six equations

for compartments (2), (3), (5), and (6), for the substance B and membranes permeable to it only. There are thus twelve fundamental equations, from which all possible combinations can be derived. My original intention had been to carry out the necessary cycles in the manner of Prof. Porter's paper (*loc. cit. ante*), but Mr. G. W. Walker pointed out to me that we are able to obtain more information by taking the compartments in pairs. A formal demonstration is reserved until such time as there is a prospect of measuring experimentally the quantities involved.

Incidentally, the following two relations between compartments (2) and (5) can be obtained directly, although they can also be derived by the previous method.

Thus, supposing both halves of the horizontal membrane to be open, pass a grammes of A and b grammes of B from (5) to (2), change the pressures to p' and $\psi_{p'}$, pass the substance back again and restore original pressures. We get

$$\int_p^{p'} s dp = a \int_{\psi_p}^{\psi_{p'}} \sigma_a dp + b \int_{\psi_p}^{\psi_{p'}} \sigma_\beta dp. \quad (2)$$

In the method by which equation (2) was derived a and b grammes of the respective components were simultaneously passed through the membrane; we can, however, get the same result by performing two cycles one after the other, thus:

Let the right-hand half-membrane be closed and perform our standard cycle by passing a gramme of A through it; we get

$$a \int_p^{p'} s_a dp = a \int_{\psi_p}^{\psi_{p'}} \sigma_a dp; \quad (3)$$

then perform a similar cycle with the left-hand half, and we get

$$b \int_p^{p'} s_b dp = b \int_{\psi_p}^{\psi_{p'}} \sigma_\beta dp, \quad (4)$$

from which (2) is at once obtained.

If $a = \alpha$, then from (3) and (4) we get

$$\int_p^{p'} s dp = \int_{\psi_p}^{\psi_{p'}} \sigma dp. \quad (5)$$

Now change the upper limits in (3) and (4) to $p' = p + dp$ and $\psi_{p'} = \psi_p + d\psi$, and we get

$$\int_p^{p+dp} s_a dp = \int_{\psi_p}^{\psi_p+d\psi} \sigma_a d\psi$$

and

$$\int_p^{p+dp} s_b dp = \int_{\psi_p}^{\psi_p+d\psi} \sigma_b d\psi,$$

from which it is easy to see that

$$\frac{s_a}{s_b} = \frac{\sigma_a}{\sigma_b} \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

This result is of theoretical interest, and may have a practical bearing on future experimental work.

A possible Connexion between the Characteristic Equations of Gases and of Solutions.

In a paper entitled "Solubility and Supersolubility from an Osmotic Standpoint" (Phil. Mag. 1912, vol. xxiv. p. 254), which will be referred to as "S and S" throughout this communication, it was shown that when either of the two osmotic pressures of a binary liquid mixture is expressed as a function of the concentration, these functions each contain a logarithm which, in the limit, becomes infinite.

Unfortunately, the proof of this proposition was but very briefly outlined, and, as the matter is of some importance for osmotic theory, it seems advisable to give a more detailed exposition.

In "Contribution to the Osmotic Theory of Solutions" * (which will hereafter be referred to as "Theory") it is shown that (using a different notation) $\delta P_a / \delta p = (z_a - s_a) / z_a$.

As the value of s_a / z_a is, in the majority of cases, close to unity, it is easy to see that the change in P_a is but a small fraction of the change in p , so that although a change in the concentration leads to a change both in p and P_a , the contribution due to the former is but small.

* Berkeley & Burton, Phil. Mag. vol. xvii. 1909, p. 604.

In this paper there are numerous errata; the more important are given below.

Page 604, equation (17), the sign governing the right-hand member should be positive.

„ 606, it should have been explained that the concentrations are differently expressed in Margule's equation.

„ 611, lines 8 and 9 from bottom, c_1/w should be w/c_1 .

„ 612, the expressions in lines 8 and 10 from bottom should be multiplied by a factor dc_2/dh .

We may, therefore, state that when the concentration a is increased, in general, the osmotic pressure P_a will decrease, whilst P_b will increase; and there are four ways in which the pressures on the liquids may be changed so as to keep osmotic equilibrium.

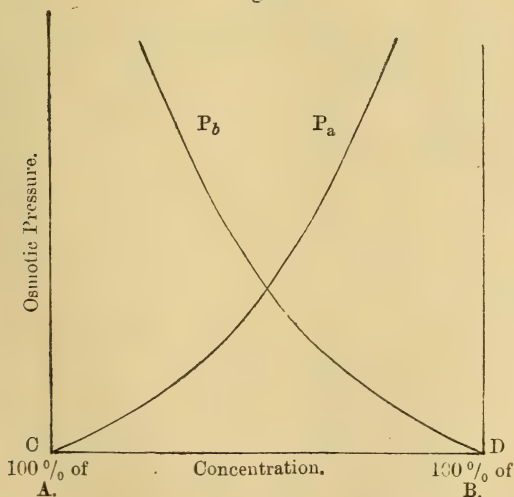
(1) Keeping p constant, p_a will increase to p_a' , and p_b decrease to p_b' , that is, P_a decreases while P_b increases. The graphs resulting from this view-point are given in the diagram of "S and S," p. 260.

(2) Keeping p_a constant, p will be decreased to p' (P_a decreases), whilst p_b will also be decreased to p_b' , but the change in p_b will be greater than the change in p (P_b increases at an enhanced rate).

(3) Keeping p_b constant, precisely the reverse of (2) will result.

(4) If we start with a system such that the three liquids are in osmotic equilibrium and impose the restriction that p_a and p_b are both to remain constant, we cannot maintain the equilibrium when the concentration is changed. We can, however, measure the osmotic pressure if one or the other of the pure liquids be shuttered off, and in this way two new sets of osmotic pressures will be obtained. Thus, in all there are four sets of complementary osmotic pressures.

Fig. 3.



Whichever scheme of viewing osmotic phenomena we adopt, the general character of the curves is that shown in fig. 3.

Theory and experiment give some information as to parts of these curves. P_a leaves C as a straight line; this is the part of the curve where for undissociated substances Boyle's law is followed; even if Boyle's law is not followed, we know from general principles that (where no chemical reaction takes place) the properties of very dilute solutions are additive, hence the straight line. Experiments hitherto have shown that for undissociated substances the curve then becomes convex to the ordinate through D. Similarly for the curve of P_b starting at D.

In "Theory," p. 604, equation (18) (but using another notation), it has been shown that for any given solution with the same pressure on it when measuring the two osmotic pressures, the relation

$$as_a(\partial P_a/\partial b)_{p_a} = bs_b(\partial P_b/\partial a)_{p_b}^* \quad . \quad . \quad . \quad (7)$$

holds between the differentials.

It has already been stated that the effect on (say) P_a of a change of pressure on the solution is but small; we may therefore consider equation (7) as applicable over a finite range of pressure, and if we assume that we are dealing with ideal liquid mixtures where s_a and s_b are independent of concentration, we can then get an idea as to what takes place in the upper part of the two curves.

Near D, $\partial P_b/\partial a$ is constant, hence $(\partial P_b/\partial a)_{p_b} = kas_a/b s_b$, but it seems reasonable to suppose that while s_a and s_b diminish with increasing pressure, they tend to a finite although small limit when p is very great, and neither vanish nor become infinite when $a=1$. Hence we have $(\partial P_b/\partial a)_{p_b} = k'a/b = k'a/(1-a)$. This on integrating within the range for which these assumptions are valid gives $P_b = C - k'[a + \log(1-a)]$, where C is a finite constant. Hence P_b becomes indefinitely great along with $-\log(1-a)$ as a approaches unity.

Similarly for P_a .

Consider now the system shown in fig. 4, where we have the pure gas B (in compartment (1)) in osmotic equilibrium through a membrane permeable to B only, with a solution of gas B dissolved in A (in compartment (2)).

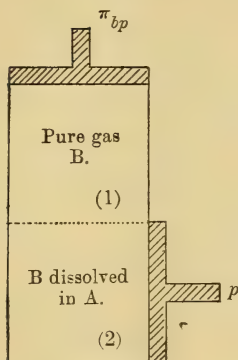
Performing the standard cycle (as already detailed) between compartments (1) and (2), the pressure limits being p and

* This relation is exact, and can be derived from equation (31) of "Theory," p. 617.

$\pi_{b\pi}$ for the solution, and π_{bp} and $\pi_{b\pi}$ for the pure gas, we get

$$\int_{p=P_a+p_a}^{\pi_{b\pi}} s_b dp = \int_{\pi_{bp}}^{\pi_{b\pi}} \zeta_b dp. \quad . \quad . \quad . \quad . \quad (8)$$

Fig. 4.



Under the conditions already discussed (p. 272) the left hand of (8) approximates to the form $-k's_b \log (1-a)$, and this imposes a restriction on the form of the characteristic equation of a gas.

Stratification and Diffusion in Mixed Vapours or Gases.—In the relation (1), if we change the limits* π_a' to

$$\psi - \Pi_a + dp - \frac{\partial \Pi_a}{\partial p} dp, \pi_a \text{ to } \psi - \Pi_a, \text{ and } \psi' \text{ to } \psi + dp,$$

we get

$$\int_{\psi - \Pi_a}^{\psi - \Pi_a + dp - \frac{\partial \Pi_a}{\partial p} dp} \zeta_a dp = \int_{\psi}^{\psi + dp} \sigma_a dp,$$

from which we derive at once

$$\frac{\partial \Pi_a}{\partial p} = 1 - \frac{\sigma_a}{\zeta_a}; \quad . \quad . \quad . \quad . \quad (9)$$

this equation is the precise analogue of (29), p. 616 of

* Subject to the restriction that for vapours the limits are less than π_{a0} , etc.

"Theory" (note that the σ_a is supposed to be measured under the *total* pressure of the mixed vapours or gases).

In a similar manner the whole of the cycle on pages 609 to 612 of "Theory" can be carried out for a column of mixed vapours (or gases); hence equations (26) and (31), pages 612 and 617, need only be translated into terms denoting the physical properties under discussion for them to be applicable.

Thus (31) is

$$\frac{dp}{d\beta} = \frac{\sigma_a}{\sigma_a - \sigma} \frac{\partial \Pi_a}{\partial p} \quad \dots \quad (10)$$

This equation must be satisfied in the solution of the problem of the stratification of two vapours or gases by gravity. This relative concentration is ordinarily evaluated* by assuming that Boyle's and Dalton's laws hold for the two components in the mixture; but equation (10) is exact, and independent of this assumption.

It may be verified that

$$\alpha \sigma_a \frac{\partial \Pi_a}{\partial \beta} = \beta \sigma_\beta \frac{\partial \Pi_\beta}{\partial \alpha} \quad \dots \quad (11)$$

holds for mixed vapours. This equation is the analogue of (18), p. 604 "Theory." If we combine (11) with (18) of "Theory" and remember that $s_a/s_b = \sigma_a/\sigma_\beta$, we get

$$\frac{\beta}{\alpha} \frac{\partial \Pi_a}{\partial \beta} \bigg/ \frac{\partial \Pi_p}{\partial \alpha} = \frac{b}{a} \frac{\partial P_a}{\partial b} \bigg/ \frac{\partial P_b}{\partial a}.$$

Conditions to be fulfilled by an Equation of State for Osmotics.

We can now state some of the conditions that appear to be required in the osmotic equation of state; thus expressing P_a as a function of b , we have the following:—

- (1) The graph of P_a near the origin is nearly linear over a finite range.
- (2) The expression for P_a must become infinite with $\log 1/b$ as b approaches zero.
- (3) As shown in "S and S," p. 260, there must be two points where $dP_a/db = 0$.

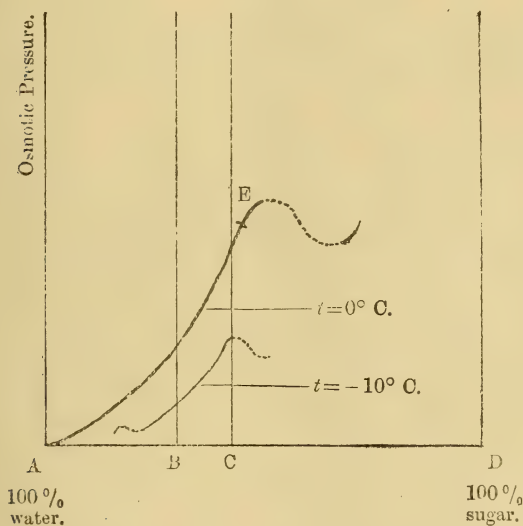
* Fundamentally in the ordinary method, Π_a is put equal to π_β (the partial pressure of the other component), and π_β is also assumed to equal π_b . It would seem that this latter hypothesis could be tested experimentally, and the experiments would be of considerable importance; but probably the discovery of suitable membranes is necessary before we can verify that $\Pi_a = \pi_\beta$.

The discussion ("S and S," p. 260) dealt with partially miscible liquids, but the main trend of the whole argument was that a valid equation of state for osmotic pressure should be such that the form is applicable both to miscible liquids and to solids dissolved in liquids.

- (4) If this be so, it will be apparent that with the latter solutions under certain conditions of temperature (and probably of pressure) there will be two more points where $dP_a/db=0$.

This is shown in fig. 5, which represents the graphs for aqueous cane-sugar solutions at two different temperatures.

Fig. 5.



The curve passing through the origin is that representing the known osmotic pressures at 0°C. The ordinate through C marks the limit of saturation (crystallizing point), and the point E is the present limit of experimental knowledge. The lower curve is the theoretical graph for -10°C. We know, however, that the saturation-point is at a concentration less than C; we also know that, when the solution is dilute, a further diminution in the concentration is followed by the freezing out of the water, so that, by analogy with what has already been postulated for the curve of super-saturated solutions—namely, that there are a maximum and

a minimum,—we should expect two more such points where the solution is supersaturated with respect to its water-content.

Hence (5) our equation of state must represent these points. (6) At the cryohydric point all these four points must coalesce into one; this also must be deducible from our equation of state. Similar arguments apply to the complementary osmotic pressure P_b .

In putting out these notes, I have had the invaluable assistance of Mr. G. W. Walker, F.R.S., to whom my best thanks are due.

XXVI. *On a Precision Method of uniting Optical Glass—the Union of Glass in Optical Contact by Heat Treatment.*
By R. G. PARKER, B.Sc., A.C.G.I., and A. J. DALLADAY*.

[Plate V.]

OWING to the numerous defects of the cements available for constructing glass cells for the examination of the optical properties of liquids, the following process, by which a much more perfect joint between two pieces of glass can be obtained, has been developed. Briefly, the surfaces of each of two pieces of glass are so worked and polished that they are either both plane or of the same curvature to a very high degree of accuracy. They can then be placed together in “optical contact,” and if they are subjected to carefully controlled heating will unite and become one piece.

In order that this method may be of any value, it is essential that the temperature at which union takes place shall not only be far below the melting-point of the glass, but also below the annealing temperature—for even at this temperature very slight strain would cause sufficient deformation of worked glass surfaces to render them useless.

It is very difficult to place the windows of a cemented cell sufficiently accurately parallel for certain work depending on the phenomena of the interference of light; parallelism to ± 1 (one) minute is only attained with considerable trouble, especially if the adhesive material requires baking to cause it to harden completely. The wedge shape of the enclosed liquid may be too great for interference work, even if the angle between the windows is not greater than a few seconds.

* Read before the Faraday Society on December 18, 1916.

In addition, cements frequently strain the materials which they hold together to such an extent that their optical properties are considerably altered. Fig. 1, Pl. V., illustrates the distortion of a glass plate 1.25 in. across, 0.1 in. thick, cemented to a piece of a brass tube by a strong and very well-known adhesive. The interference-rings are produced between the plate and a proof-plane of quartz; the plate was originally very flat, and showed less than one interference-ring across its entire face. After cementing, the series of rings appeared, indicating a depression in the centre of the plate of about $\frac{1}{5000}$ in. There appears to be considerable force acting radially inwards; such distortion would render the glass plate useless for almost any accurate optical instrument, especially if polarized light were passed through it or interference-phenomena were being observed.

Glass surfaces can be polished without difficulty so nearly flat—or so nearly of the same curvature—that, when carefully cleaned and freed from dust, they show less than one interference-fringe per inch when placed together and examined by light reflected from the interfaces. Such surfaces can be pressed into optical contact by the application of pressure of several pounds per square inch, and the pieces of glass act as one for optical purposes: for example, if the hypotenuse of a 45° prism is in such contact with another piece of glass, no total reflexion—indeed, no reflexion at all—is obtained from the common surface. They can easily be separated by sudden warming or cooling, by force, if applied in a *peeling* manner, and by liquids; the latter gradually creep in and lift the surfaces apart. The joint is very resistant to forces tending to slide one surface over the other.

A cell constructed of two plates of glass in optical contact with a U-shaped separating piece would have the advantages of great accuracy of parallelism between the windows; very little strain in the windows if the components were of one kind of glass and put together at the same temperature; and an “all glass” construction, involving no cement to contaminate liquids placed therein, and to perish eventually under the action of solvents or corrosive substances. But it would be quite useless, owing to the ease with which such surfaces can be separated by the methods described above.

It is well known that if glass is heated it gradually becomes less viscous as the temperature rises, passing through all degrees of viscosity until at a high temperature it is quite mobile; there is thus no sharp melting-point, but only an approximate position which varies from about 1000° – 1400° C.

At temperatures very much below the melting-point the glass is still liquid enough to deform gradually under stress—hence the slow permanent bending of a glass rod supported at each end, in a horizontal position, and at ordinary temperatures. Glass behaves, in fact, as a brittle elastic solid under sudden strain, but as a viscous liquid to severe strain applied over long periods when at ordinary or moderately elevated temperatures; with rise of temperature the elastic nature of the glass becomes more and more masked by the decrease in viscosity; and at a temperature approximating to the melting-point it becomes no longer observable.

Annealing Temperature.—If a piece of glass having two plane, parallel, and polished sides is placed in an electric furnace so that it can be heated and examined by transmitted polarized light at the same time, the strain caused by unequal heating can be observed both as regards position and intensity by its effect on the light. This strain, which would be very evident at lower temperatures in a piece of glass in the form of a $\frac{1}{2}$ -inch cube, or larger, suddenly disappears over quite a short range of temperature situated very much below the melting-point. The glass has obviously reached a temperature at which it is sufficiently mobile to accommodate itself rapidly to the stresses caused by unequal heating—it is therefore deformed, and the stress disappears; this is clearly the annealing-point, in that a piece of badly annealed glass would lose all internal stress at this temperature, and if sufficiently slowly cooled would be perfectly annealed.

Relation of the Temperature employed to the Annealing Temperature.—The viscosity of a glass at its annealing temperature is still very great, but it has softened sufficiently for a pointed tool, pressed against it with considerable force, to make its way slowly in. Therefore, an optically worked surface of a piece of glass would not retain its form accurately after heating to the annealing temperature, if some clamping apparatus had touched the surface.

The mobility of glass has been found to be an exponential function of the temperature

$$S_T = S_{T_1} A^{\frac{T-T_1}{N}},$$

where S_T, S_{T_1} are the “mobilities” at the temperatures T, T_1 , measured by the rate of deformation of glass under constant stress, and A and N are constants for the glass. The quantity N is comparatively small, so that for quite small values of $T - T_1$, the index $\frac{T-T_1}{N}$ would become equal to 1, 2, 3 ... If, for example, we take $N=8$, $A=2$, and compare the

values of the mobility of the particular glass at temperatures of $T=560^{\circ}$ C. and $T_1=552^{\circ}$ C., 544° , 536° successively, we find the respective values of the mobility to be

$$\begin{aligned}\frac{S_T}{S_{T_1}} &= 2^1 && \text{when } T_1 = 552^{\circ} \text{ C.} \\ &= 2^2 = 4 && \text{when } T_1 = 544^{\circ} \text{ C.} \\ &= 2^3 = 8 && \text{when } T_1 = 536^{\circ} \text{ C.}\end{aligned}$$

That is, the glass becomes twice as "soft" for *every* rise of temperature of 8° C. Therefore, at 60° or 70° C. below the annealing temperature a glass has become sufficiently hard to withstand very great local pressure for short periods without sensible deformation. The method of determining the annealing temperature will be described at a later date; it should be known accurately for each kind of glass which is to be joined, as by this means only can we obtain a sufficient welding effect together with the minimum risk of injury to the surfaces.

Working at this temperature, 60° C. below the annealing-point, two pieces of glass under pressure and in optical contact will unite perfectly in less than 1 hour. At the same time the deformation of the outer surfaces, caused by the imperfections in the plates compressing them, is so very slight that a few strokes on a polishing tool are all that is necessary to restore them to the condition of optical surfaces of high accuracy—or treatment of the surfaces may be altogether unnecessary. It is perhaps well in practice to work at a temperature 10° – 20° below this maximum safe temperature in order to ensure that no deformation shall occur.

Methods of distinguishing between Optical Contact and Complete Union.—With regard to tests for distinguishing perfect union, we have already noted that the optical contact of two surfaces is easily destroyed by sudden temperature change, by the action of liquids, and by mechanical force; when the contact has changed into complete union, they cannot be separated by any of these means, and if force is used the two pieces of glass break as one—not along the interface. A crack or a diamond-cut spreads through the two pieces as though one piece of glass, whereas if the pieces are merely in ordinary optical contact, it cannot be made to pass from one to the other; this is well shown in figs. 2 and 3 (Pl. V.), and is a most conclusive proof of the completeness of the joining.

EXPERIMENTAL.

The temperature selected for our experiments on the union of glass surfaces was considerably below the annealing-point, in accordance with the facts already discussed. Two preliminary experiments were made, using a metal box having 7 in. sides, filled with sand and heated by gas-burners. Pieces of crown glass, $5 \times 5 \times 1.5$ mm. were put into contact, wrapped in asbestos-wool and held together by a clamp; they were then heated at the rate of 1° C. per minute to a probable maximum of 400° – 450° C., maintained at this temperature for 1 hour, and slowly cooled.

They were found to have united, but not completely. When torn apart with considerable force each piece carried with it glass from the other. All the surfaces were optically perfect after heating (fig. 4, Pl. V.).

In the second experiment larger pieces (1 in. in diam., $\frac{1}{8}$ in. thick) of different kinds of glass were employed—crown and heavy flint. Heating was as before, but rather more vigorous; probable maximum temperature 450° – 500° C. The glass was clamped between pieces of brass plate, with asbestos packing. The disks united at one place only; here the joining was perfect, and when they were forced apart the flint carried with it a portion of the crown over the whole of this area. The external surface of the flint glass was spoiled, as it had softened slightly; the crown glass was almost uninjured.

These experiments having proved that joining would take place, more careful ones were conducted with a view to constructing apparatus by the method.

A platinum-wound electric-tube furnace (internal dimensions $3\frac{1}{2}$ in. \times $2\frac{1}{2}$ in., 14 in. long) was fitted with double silica windows at each end. It was controlled by two resistances in series. One, the main resistance, was used to compensate for the very great changes in the resistance of platinum which take place between 20° C. and 600° C.; the second permitted of much more gradual changes of resistance, and formed the fine adjustment in this respect. The temperature at any instant was known by means of a platinum resistance thermometer, allowance being made for any lag in its indications; and, further, the thermometer was connected to a Callendar recorder, giving a permanent record of the temperatures used in any experiment, and enabling the *rate of change* of temperature to be seen at a glance.

The heating and cooling were therefore completely under control, and a continuous temperature change as small as $\frac{1}{4}^\circ$ C. per minute could be maintained indefinitely.

An arrangement by which polarized light could be passed

through the furnace, and examined after passing through the piece of glass or silica under test, completed the apparatus. By this means the effect of unequal heating caused by rise or fall of temperature could be observed, and if necessary the actual stresses set up in any part of the test piece could be calculated at any time during or after the experiment.

Three plates, all of a hard crown glass, were put into optical contact, the centre one being about 10 mm. thick, and drilled so as to give a cell suitable for the comparison of two liquids, as in the Rayleigh interference-refractometer. The outer plates were, of course, merely windows of about 3 mm. thickness. The cell was heated without pressure in the electric furnace at the rate of 2° C. per minute to 460° C., and after two hours at this temperature it was cooled at 4° – 5° C. per minute; the arrangement of the furnace permitted continuous inspection of the cell. During heating, at 200° – 300° C., minute imperfections in the contact grew rapidly, one side of the cell coming almost completely away. When cold it was found to be out of contact over parts of the surface, the rest of the surface being in contact, but covered with spots.

Rapid temperature-changes, such as would easily have separated glass in ordinary contact, had no effect; water also failed to lift the surfaces apart; and when a thin knife-blade was forced in from a corner where the two surfaces were apart, the portion of the window out of contact was broken off without moving the window as a whole. The cell was then compressed in a vice in such a way as to apply large shearing stresses at the interfaces, with the result that corners of the windows out of contact broke away, while the rest, in contact, remained unchanged. The cell then appeared as shown (fig. 5, Pl. V.).

The spots referred to were small round areas where the surfaces were just out of contact. Each developed from a minute flaw in the optical contact of the surfaces, and when examined microscopically very minute black particles could be seen in each, and from the system of Newton's rings apparent in them during the heating they appeared to contain a gas at high pressure—by the same means the pressure was observed to diminish slowly after a spot had spread outwards to one edge of the cell; and, finally (in a later experiment), when the temperature was raised above the annealing-point, the walls of each spot were slightly but definitely blown out, so as to appear convex from the outside. It therefore appears that the spots are due to the decomposition of minute

particles of cellulose from the rag used in cleaning the surfaces; a pressure of many atmospheres can be produced in this way. By careful cleaning it is possible to eliminate them almost entirely. Cells which have comparatively large areas in contact are less free from spots than those in which no point is far from an edge; the gases which would remain permanently enclosed in the former are able to escape from the latter, and the surfaces then go back into complete contact.

The optical surfaces of this cell were found to be perfect and quite unchanged after heating, including the unsupported internal surfaces; we therefore have *optically worked* surfaces in the *interior* of a solid glass cell. In fig. 5 it will be seen that an area at X is completely out of contact except for a narrow arc formed round the drilled aperture. This is clearly shown in fig. 6 (Pl. V.), under a magnification of six diameters. It is not well known that ground-glass surfaces act as if they were in compression: thus, a thin plate originally flat and polished on both sides becomes, when finely ground on one side, a concave mirror of long focus on the other. In the case of our cell, the rough surfaces of the drilled holes push up a burr round the edge which is only a few wave-lengths high, but sufficient to prevent complete optical contact. This burr was therefore removed by "retouching" on a polisher, but traces of it evidently remained, and by producing local pressure caused the union to be very complete over its surface. Severe strain was applied by forcing a thin wedge between the two surfaces without breaking this narrow area of complete union. The same effect was also shown by another corner of the same cell which was out of contact after heating and was broken off; the fracture travelled round the edge of the drilled hole instead of passing straight across it (Pl. V. fig. 7 and fig. 5 at Y).

A second cell was then made of the same glass and pattern, and heated at the rate of 1° – $1\frac{1}{2}^{\circ}$ C. per minute to a temperature nearer the annealing-point— 523° C.,—at which it was kept for two hours, then cooled at 4° – 5° C. per minute. Pressure was applied by means of a hand screw-clamp. Two brass plates, with surfaces ground flat, and sufficiently thick to eliminate bending ($\frac{1}{4}$ in. thick), were used to distribute the pressure; a few thicknesses of thin paper were placed between the brass surface and glass surface to take up minute irregularities—the carbonization of the paper did not interfere with its action.

The union of the three components was complete except for a few small spots. They could not be separated by any

of the means indicated, and when subjected to severe mechanical strain a portion of the cell broke away, showing the conchoidal fracture of a solid glass block. No bending of the fracture occurred at the interfaces, except at one small portion where a spot showed that there was no contact (fig. 3, Pl. V.).

The optical surfaces had all remained perfect as regards plastic deformation. The outer surfaces were slightly corroded by the paper-ash, and had to be repolished. When examined by means of a Babinet compensator (for the effect on polarized light), very little internal stress was observed, in spite of the unnecessarily rapid cooling; the maximum stress indicated was about 150 lb. per square inch. This amount could easily be decreased, but is already negligible for most purposes.

A third cell of rather different construction (fig. 8, Pl. V.) showed very few imperfections of contact. Heating was carried out exactly as in the previous case, *i. e.* at 90° C. below the annealing-point. The areas in contact are all narrow, and no point is more than $2\frac{1}{2}$ mm. from an edge. Any centres of gas-pressure developed in the way already described are therefore likely to disappear owing to escape of the gas, and we find in general that these narrow areas give the most perfect joining.

The glass of the cell showed very little strain, although no special precautions, such as annealing, were taken. By avoiding temperature-differences when putting the components into optical contact, and by subsequent slow cooling from the annealing temperature, all traces of strain can be eliminated.

The internal surfaces of the cell-windows were parallel to 1 second both before and after union. The degree of parallelism remained quite unaltered, and it therefore appears that the accuracy of parallelism is determined only by the initial accuracy of the central component.

Union of Two Different Kinds of Glass.—The components of the cells described above were all made of one kind of glass, and the joining of different glasses is complicated by at least three factors—differing expansion coefficients, differing annealing-points of the glasses, and the degree of ease with which they will fuse together in the blowpipe-flame. The first will certainly cause the surfaces to come apart while the temperature is rising, but if they are under pressure at about 30 lb. per square inch this should not greatly matter, as they will go into contact when the temperature is constant at its highest limit, and they will then join perfectly. Strain

will appear owing to different contraction as they cool, now as one piece, but for some purposes it may not matter. Such strain as this cannot be obviated by "annealing." Difference in the annealing-points is the more exacting factor, for unless the annealing-points of the glasses to be joined are fairly close (within perhaps 50° C.) the more fusible one will reach its annealing-point before the less fusible reaches a temperature at which it will unite with another glass in any reasonable time. The annealing-points of glasses in common use may differ by 200° C. or even 250° C., and it is obvious therefore that many pairs of glasses could be selected which would be very difficult or impossible to join; on the other hand, for most purposes suitable glasses can be chosen. With regard to the last factor, it appears that certain kinds of glass which will not fuse together readily in the blowpipe-flame will also not unite by the new method.

A Rayleigh cell prepared of hard crown glass with plate-glass windows was heated to a low temperature— 400° C.—at the rate of 2° – $2\frac{1}{2}^{\circ}$ C. per minute and kept at the maximum temperature for $1\frac{1}{2}$ hours. Pressure was not applied. In consequence of this, and also of the different temperature expansion coefficients, they remained in optical contact only over a very small part of the surfaces. When cold the glass was found to have united in these places in spite of the unnecessarily low temperature. The areas of contact were so small that the windows could be forced off without fracture, and they then carried with them glass from the other component. The optical surfaces had not been changed by the heating.

This experiment (as well as that described above) indicated that two glasses of quite widely differing annealing-points could be joined even under unfavourable conditions.

A more severe test was then carried out with an object-glass having curves of the same radius on the common faces of its components. The annealing-points of the two glasses employed (flint and crown glass) differ so widely, it was thought advisable to heat approximately to the annealing temperature of the softer glass. The lenses, in optical contact, were clamped together at the edge at three equidistant points, then heated at 1° – $1\frac{1}{2}^{\circ}$ C. per minute to a maximum temperature of 476° C. They remained so for 1 hour and then cooled at 4° C. per minute. They were then completely out of contact, except under the three points at which pressure had been applied; in these places there was perfect union. The flint lens had softened to such an extent that slight dents had been made in its surface by the clamp. Both

lenses were found to be strained when examined by polarized light. A few spots which had developed in the usual way from minute dust particles had blown out into flat bubbles in the flint glass, indicating that they contained gas under great pressure, as we had already inferred.

It appears, therefore, that the flint and crown glasses commonly used in object-glasses differ too widely in annealing temperatures for successful union. Owing to the large number of factors which limit the nature of the glasses to be employed, this is one of the most difficult cases to which the method has been applied.

Polarimeter Tubes.—A polarimeter tube having windows permanently fixed in position by this method was prepared without difficulty. The tube was of soda-lime glass and the windows of plate glass; maximum temperature 470° C. The joint was perfect, and in spite of the fact that different glasses were employed, the windows showed little strain—the amount was found not sufficient to interfere with measurements of rotation in any way (see figs. 9 and 10, Pl. V.). For many purposes this form of tube should be very convenient, especially in respect of ease of cleaning and freedom from corrosion. As soon as possible we intend to apply this construction to jacketed tubes; they would somewhat resemble the ordinary pattern of glass Liebig condenser, and should, with careful heating, withstand very high temperatures. The nature of the hot circulating liquid would be determined only by the temperature required, and not by the powers of resistance of the cement, as is the case at present.

Union of Fused Silica.—An experiment with component parts of this material showed that there was no essential difference between its behaviour and that of glass; the temperature required for union was naturally found to be much higher. The upper limit of temperature to which silica glass apparatus may be heated is determined by its power of devitrifying; this takes place at about 1200° – 1300° C.*, and is accompanied by great decrease in mechanical strength. It is obvious that a very small amount of devitrification would be sufficient to spoil silica glass for optical work, especially as it takes place more readily where there is access to the air, *i. e.* at the surfaces. The highest temperature which we can use is therefore somewhat below 1200° C.; fortunately a preliminary experiment has shown that a still lower temperature will suffice.

* Blackie, Trans. Faraday Soc. vii. p. 158 (1911); Crookes, Proc. Roy. Soc. A. lxxxvi. p. 406 (1912).

The annealing temperature of silica was not determined, as the small temperature expansion coefficient and good heat conductivity rendered it somewhat difficult to produce observable strain by heating in the small pieces of transparent silica which were available.

Two plates of silica glass 0.75 in. \times 0.5 in. \times 0.1 in. were put into optical contact with the ends of a silica ring 1.0 in. diam. and 0.5 in. long, in order to make a small cell suitable for investigating the ultra-violet absorption spectra of liquids. This was held in a steel clamp, with a few thicknesses of paper inserted between the steel and the silica, and heated to 1030° C. for 1 hour.

While cooling, contraction of the clamp fractured the cell, but portions of it, examined when cold, were found to have joined. On forcing them apart some of the material of the plate was torn away by that of the ring, and *vice versa*; from the nature of the union we judge that a rather higher temperature, probably in the neighbourhood of 1100° C., will be required to give results equal to those attained with glass. The planeness of the silica plates was found to be unchanged.

In conclusion, we wish to thank Mr. F. Twyman, of Messrs. Adam Hilger, Ltd., for continued help and many suggestions.

Research Laboratories,
Adam Hilger, Ltd.

XXVII. *On the Energy in the Electromagnetic Field.*

To the Editors of the Philosophical Magazine.

DEAR SIRS,—

The University, Sheffield,
February 2nd, 1916.

IN your issue of last month * Mr. E. A. Biedermann discusses some consequences of the assumption that the magnetic or kinetic energy density in the electromagnetic field is $\mathbf{H}^2/8\pi$, and as the outcome of this discussion he proposes a modified form for this expression, viz.:

$$\frac{1}{8\pi} \{ \mathbf{H}^2 + (\text{div } \mathbf{A})^2 \},$$

\mathbf{H} being the magnetic force vector and \mathbf{A} the magnetic vector potential.

As this new form of expression for the density would carry with it all the mathematical and physical uncertainties involved in any theory interpreted in terms of the scalar and

vector potentials and arising from the incompleteness of the definitions of these potentials, it must not be allowed to stand without a strict scrutiny of the reasons for its introduction. A careful examination of Mr. Biedermann's argument will, however, soon show that his evidence of justification is convincing only for the special case when $\text{div } \mathbf{A} = 0$, when the modified expression is equivalent to the older one.

Mr. Biedermann commences by an examination of the field of a number of very small spherical surface charges, the typical one of which, with charge e_s and radius a_s , may be taken with its centre at the point (x_s, y_s, z_s) and to be moving with the comparatively small velocity v_s . The electric force at the point (x, y, z) in the field is then derived as the gradient of the scalar potential

$$\phi = \sum \phi_s = \sum \frac{e_s}{r_s},$$

where

$$r_s^2 = (x - x_s)^2 + (y - y_s)^2 + (z - z_s)^2;$$

whilst the magnetic force is

$$\mathbf{H} = \frac{1}{c} \sum [\mathbf{v}_s \mathbf{E}_s], \quad \mathbf{E}_s = -\text{grad } \phi_s,$$

the notation denoting the vector product, and c is the velocity of radiation: this last vector may also be derived as the *curl* of the vector potential

$$\mathbf{A} = \frac{1}{c} \sum \frac{e_s \mathbf{v}_s}{r_s} = \sum \frac{\mathbf{v}_s \phi_s}{c}.$$

The potential energy in the field, when the motions are slow enough, is then

$$\begin{aligned} \frac{1}{8\pi} \int \mathbf{E}^2 dv &= \frac{1}{8\pi} \int dv \{ \sum \mathbf{E}_s^2 + 2 \sum (\mathbf{E}_s \mathbf{E}_{s'}) \} \\ &= \frac{1}{2} \left\{ \sum \frac{e_s^2}{a_s} + 2 \sum \frac{e_s e_{s'}}{r_{ss'}} \right\}, \end{aligned}$$

where

$$r_{ss'}^2 \equiv (x_s - x_{s'})^2 + (y_s - y_{s'})^2 + (z_s - z_{s'})^2.$$

The kinetic energy is, on the other hand, equal to

$$\begin{aligned} \frac{1}{8\pi} \int \mathbf{H}^2 dv &= \frac{1}{8\pi c^2} \int dv \{ \sum [\mathbf{v}_s \mathbf{E}_s]^2 \} \\ &= \frac{1}{8\pi c^2} \int dv \{ \sum [\mathbf{v}_s \mathbf{E}_s]^2 + 2 \sum ([\mathbf{v}_s \mathbf{E}_s] [\mathbf{v}_{s'} \mathbf{E}_{s'}]) \} \\ &= \frac{1}{8\pi c^2} \int dv \{ \sum v_s^2 \mathbf{E}_s^2 + 2 (\mathbf{v}_s \mathbf{v}_{s'}) (\mathbf{E}_s \mathbf{E}_{s'}) \} \\ &\quad - \frac{1}{8\pi c^2} \int dv \{ (\mathbf{v}_s \mathbf{E}_s)^2 + 2 (\mathbf{v}_s \mathbf{E}_{s'}) (\mathbf{v}_{s'} \mathbf{E}_s) \}. \end{aligned}$$

The first integral in this last expression is obviously equal to

$$\frac{1}{2c^2} \left\{ \sum \frac{e_s^2 \nu_s^2}{a_s} + 2 \sum \frac{e_s e_{s'} (\nu_s \nu_{s'})}{r_{ss'}} \right\},$$

whilst in the second it is easy to verify that

$$\int (\nu_s E_{s'}) (\nu_{s'} E_s) dv = \int (\nu_s E_s) (\nu_{s'} E_{s'}) dv;$$

so that it is equal on the whole to

$$\frac{1}{8\pi c^2} \int \{ \sum \nu_s E_s \}^2 = \frac{1}{8\pi} \int (\text{div } A)^2 dv.$$

Thus, finally, we have

$$\frac{1}{8\pi} \int \mathbf{H}^2 dv = \frac{1}{2c^2} \left\{ \sum \frac{e_s^2 \nu_s^2}{a_s} + 2 \sum \frac{e_s e_{s'} (\nu_s \nu_{s'})}{r_{ss'}} \right\} - \frac{1}{8\pi} \int (\text{div } A)^2 dv,$$

which is equivalent to the formula obtained by Mr. Biedermann, although the present deduction is somewhat simpler.

This result is now applied to the case of two linear conducting circuits when the current in each is the same all round—that is, when the conditions are those of an equilibrium theory. In this case we must assume that $\text{div } A = 0$ at all points of the field; so that the outstanding integral in the general reduction vanishes, and the distribution of the kinetic energy with the density $\mathbf{H}^2/8\pi$ in the surrounding field is equivalent to the expression

$$T = \frac{1}{2c^2} \left\{ \sum \frac{e_s^2 \nu_s^2}{a_s} + 2 \sum \frac{e_s e_{s'} (\nu_s \nu_{s'})}{r_{ss'}} \right\},$$

as it must be in order that the correct value for the mutual potential of the two circuits may be obtained.

In the more general case, however, there is no general warrant for the assumption that $\text{div } A = 0$; but then the use of the expression T for the kinetic energy is not legitimate. By assuming that it is, Mr. Biedermann tacitly neglects the interaction between the electric and magnetic fields in the æther; for it is just this action which gives rise to the outstanding term in the ordinary expression for the integral in the special case under investigation. This may best be seen by transforming the integral for the kinetic energy into the form

$$\frac{1}{2c} \int (AC) dv,$$

where C is the total current defined in terms of the magnetic force by Ampère's relation,

$$\frac{4\pi}{c} C = \text{curl } \mathbf{H};$$

it thus consists of the part

$$\frac{1}{2c} \sum e_s (v_s A)$$

due to the electronic motions, and the part

$$\frac{1}{8\pi c} \int \left(A \frac{dE}{dt} \right) dv$$

due to the æthereal current. Since

$$\mathbf{E} = -\frac{1}{c} \frac{d\mathbf{A}}{dt} - \text{grad } \phi, \quad \text{div } \mathbf{A} = -\frac{1}{c} \frac{d\phi}{dt},$$

we have

$$\frac{1}{8\pi c} \int \left(A \frac{dE}{dt} \right) dv = -\frac{1}{8\pi c^2} \int \left(A \frac{d^2 A}{dt^2} \right) dv - \frac{1}{8\pi c} \int (\mathbf{A} \nabla) \frac{d\phi}{dt} \cdot dv.$$

Now in an equilibrium theory the first integral on the right vanishes, and the second transforms by integration by parts to

$$\begin{aligned} & \frac{1}{8\pi c} \int \frac{d\phi}{dt} \cdot \text{div } \mathbf{A} \, dv \\ &= -\frac{1}{8\pi} \int (\text{div } \mathbf{A})^2 dv, \end{aligned}$$

as above.

An exactly similar criticism also applies to the assumption of the general validity of the form

$$\frac{e_s e_{s'}}{r_{ss'}}$$

for the mutual potential energy of two charges. The only really consistent value for the potential energy in the field in the most general case is

$$\frac{1}{8\pi} \int E^2 dv;$$

and this can easily be shown by a similar argument to contain the part

$$-\frac{1}{8\pi c} \int \left(E \frac{dA}{dt} \right) dv$$

due to the æthereal conditions.

The method employed by Mr. Biedermann for the generalization of his theory to allow for propagation effects is very ingenious, but hardly susceptible of strict mathematical specification. The assumption of a finite velocity of propagation involves the further assumption of a reacting agent to effect the propagation; and no theory of the interaction of radiating particles can be valid if it does not take account of the action of this agent and its associated energies.

I am,

Yours very truly,
G. H. LIVENS.

XXVIII. *The Scattering of α Particles by Gases.* By R. R. SAHNI, M.A., Professor, Government College, Lahore*.

[Plate VI.]

AS mentioned in a previous paper†, the writer was engaged for the best part of a year at the Physical Laboratories of the University of Manchester, on the determination of the scattering of α particles in their passage through gases. The method adopted consisted in allowing α particles from the tip of a very fine needle activated with radium C to pass through a small hole (about $70\ \mu$ in diam.) made in a platinum diaphragm, and then to strike a photographic plate placed in a suitable chamber at a known distance. The chamber contained the gas with which experiments were to be conducted at a known pressure. The photographic plate was exposed to the particles for a period varying from two to three hours and then developed. The plate was then examined under the microscope and the distribution of the silver grains in equal concentric areas from the centre of the image outwards was determined and recorded.

Some forty plates were prepared in this manner, with the apparatus finally adopted. The detailed examination of the plates was reserved till after the writer's return to India towards the close of last year. Unfortunately many of the plates were found spoiled, and the remaining ones, while giving promising results, are not considered to afford sufficient experimental data from which the angle of scattering could be calculated with any approach to certainty.

As it may be some time before the experiments can be repeated with radium C, it is considered advisable to publish this preliminary paper on the work already done. Meanwhile,

* Communicated by Sir E. Rutherford, F.R.S.

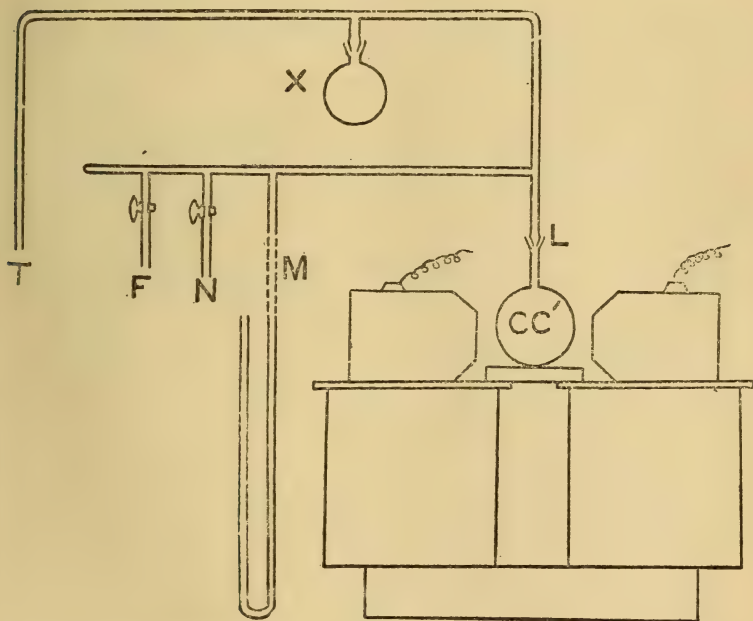
† Sahni, Phil. Mag. June 1915.

the experiments are being continued both with gases and metal foils with thorium active deposit as the source of α particles, though it must be stated that, owing to lack of intensity, thorium active deposit did not give very encouraging results with gases in some preliminary experiments carried out at Manchester. With the heavier metal foils, however, they will probably give even more satisfactory results than those obtained by Geiger by the scintillation method.

Description of Apparatus used.

Figs. 1 and 2 will explain the arrangement of apparatus as finally adopted. CC is the gas-chamber shown in fig. 2. The gas chamber is connected by (fig. 1) a glass tube with a Toepler pump at T, a Fleuss pump at F, a manometer at M,

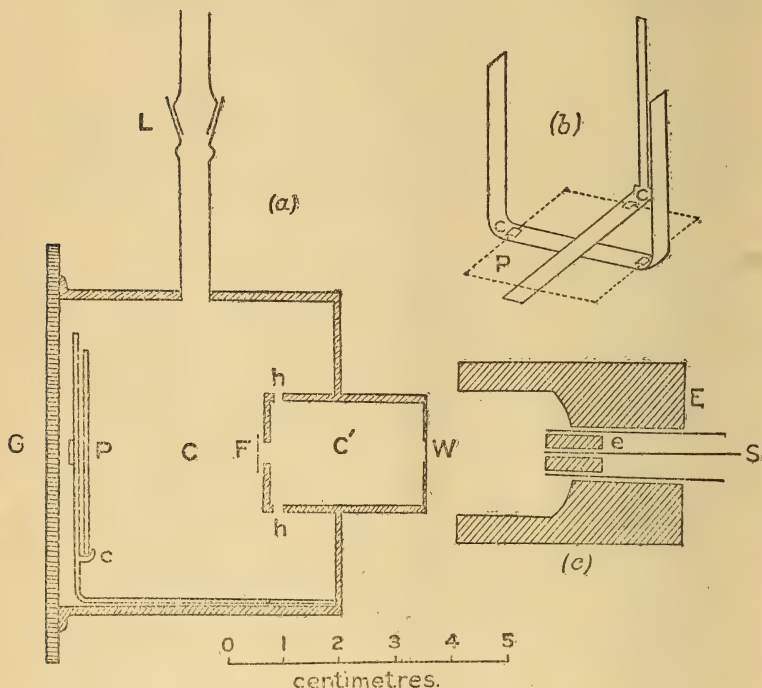
Fig. 1.



a small flask containing P_2O_5 at X, and a side-tube at N communicating with a series of drying-tubes through which any particular gas can be admitted into the gas-chamber. At L is a ground-glass joint where the gas-chamber can be readily connected to or detached from the rest of the apparatus. The gas-chamber is placed between the poles of an electromagnet to deflect β rays.

Fig. 2 (a) represents the gas-chamber. It is made of metal with the left end open. The rim of this end is provided with a carefully ground flange, so that the slate G can easily be fixed on to it air-tight with a little grease, as shown in the diagram. At the other end, the chamber has a tube C' also of metal passing through the lid as seen in the figure.

Fig. 2.



The tube C' has two small holes, one at each end, 2-3 mm in diameter. The hole at the outer end is closed by means of a thin sheet of mica, the stopping-power of which is equivalent to about 1.5 cm. of air. This forms a small mica window W through which the active particles are shot into the chamber from a source placed next to the mica. The hole at the inner end of C' is covered by a small piece of platinum foil with a fine pin-hole F in the centre of it. In addition, there are three or four larger holes in the sides of the tube C' as shown at h, h. These are provided to facilitate the exhaustion of the whole chamber C C', and to prevent too much pressure being exerted during the process on the platinum foil. The distance $FW = FP = 3$ cm. It is necessary

to make the hole as small as possible. In the apparatus finally adopted it measured $70\ \mu$, but it can be made smaller still.

(b) is the plate holder. It is made of two brass strips bent and soldered together as shown. Three little catches *c, c, c* serve to keep the plate *P* in position. The three legs of the holder are of such a length that when the holder is pushed into *C* (fig. 2), the distance between the hole *F* and the photographic film is always exactly 3 cm. After the holder with the plate fixed in position has been introduced, the open end of *C* is closed by the slate *G*.

(c) represents in longitudinal section a holder for the active source *S*. It consists of an ebonite piece *E* in which a brass tube fits closely and, in turn, carries a small ebonite cylinder *e*. The latter is perforated by a narrow canal just wide enough to admit the active needle. The whole apparatus is made to fit like a cap on the outside of *C'*. The needle is fixed in the small ebonite rod *e* in such a position that the active tip is just within the end of the brass tube. After the active needle has been fixed in position, the brass tube should project several millimetres within the hollow of the outer ebonite *E* (that is, as shown in the diagram). When *E* is pushed over *C'*, the brass tube will be pressed back to the necessary extent.

This elaborate form of holder for the active source was necessary in order to ensure that the needle may be fixed in position with the active point exactly opposite the hole *F*, and almost in contact with the mica window, within a few seconds. A small paper cap was always put over the active end so that the point only projects to about the same extent through a hole in the cap. It will be seen the active source is placed *outside* the gas-chamber. The emanation which is known to cling to the active point for a considerable time is thus kept away from the photographic plate. The needle-point was activated by exposing it to about 30 millicuries of radium emanation for the necessary period of time. It was inserted in the holder a quarter of an hour after withdrawal from the emanation-tube. The method of carrying out the experiment is explained by the arrangement of apparatus already discussed. As a rule, the plates were developed immediately after exposure; occasionally an unexposed plate was also developed along with the exposed plate to serve as a control.

Examination of the Plates.

A naked-eye examination of the photographic plates prepared with any particular gas at different pressures showed that while with a pressure of a few millimetres the impression

on the developed plate was a small and dense spot, with increasing pressures it became larger and at the same time less and less dense. The impression at very low pressures was almost uniformly dark except at the extreme edges, but with higher pressures there was a gradual falling off in the density of the impression from the centre outwards. With different gases the size of the impression under similar conditions was different. Plate VI. A, B show microphotographs of two impressions obtained with air: A under a few mm. pressure, and B under 161 mm. The two impressions were taken under conditions which were otherwise similar, and both have been enlarged to the same extent. They bring out in a fairly striking manner the differences just noted.

Method of counting the Silver Grains.

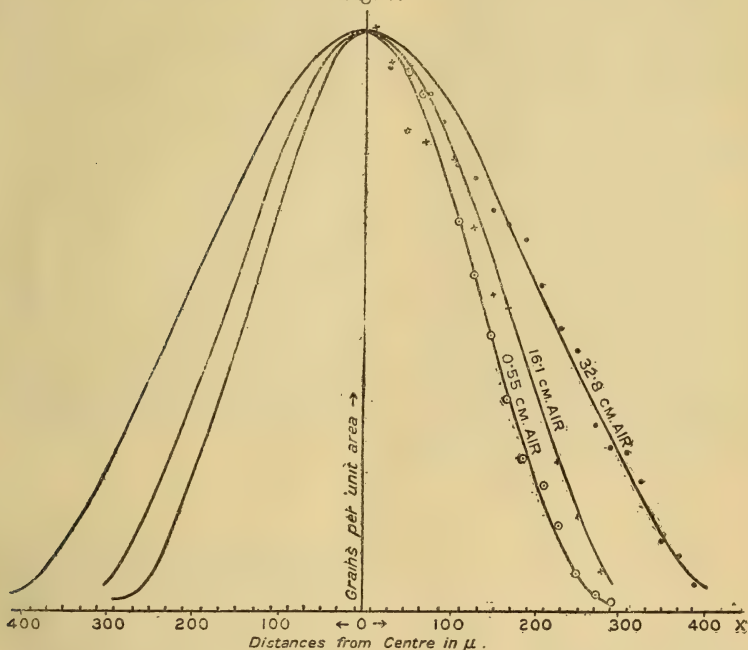
For counting the grains, a microscope with $\frac{1}{6}$ in. objective and $\times 8$ eyepiece were used. The eyepiece was provided with a micrometer in squares, so divided that each square covered exactly 400 sq. μ of the magnified object. A thin sheet of mica with two very fine cross-lines scratched on it was placed on the photographic plate with the crossing of the lines exactly over the centre of the image, this adjustment being first made roughly with the naked eye, and afterwards more accurately with the help of the microscope. The number of grains in each square of the eyepiece micrometer along one line from the centre outwards was then noted, the plate being shifted along that line as the periphery of the image was approached. The scratched lines over the mica are too far out of focus to interfere with the counting, while, at the same time, serving as reliable guides. In order to protect the photographic film from dust and scratches, it is important to cover the impression with a drop of Canada balsam and a thin glass coverslip as soon as the film is dry. The want of this simple precaution cost the writer the loss of several valuable plates. The use of an oil-immersion lens was found undesirable for several reasons. Besides greatly increasing the labour of the counting, it actually multiplies the chances of error in the process. For, whereas in the case of the $\frac{1}{6}$ in. objective the grains at different levels in the film are nearly all visible at one focus, with a $\frac{1}{12}$ in. objective they require different adjustments, and very often it becomes difficult to say whether a particular grain has been already recorded, unless all the grains are first drawn by means of a *camera lucida* and then counted.

The centre of the impression having been adjusted carefully in the manner already explained, the number of grains seen within successive equal areas of $20 \times 20 \mu$ are counted from

the centre outwards along four radii 90° apart. The averages of the four equal areas at the same distances from the centre were taken.

Some typical results are shown in fig. 3 for the case of air,

Fig. 3.



the left-hand part of the curve as shown being simply a replica of the right-hand part. The general distribution of the particles for different air-pressures can be seen from the figure, but the results are not sufficiently accurate to deduce the most probable angle of scattering with any certainty.

The primary intention of the investigation was to determine the scattering in hydrogen, which is even smaller than in air. This problem has not yet been solved, but in view of the necessity of discontinuing the experiments, it was thought of interest to indicate a method which shows good promise of success.

In conclusion, the writer desires to express his indebtedness to Drs. W. Makower and N. Bohr for their kind help and guidance in carrying out the research. He is also thankful to Sir Ernest Rutherford for allowing him to carry out the above experiment in the Physical Laboratory of the University of Manchester as well as for his kind interest and advice.

XXIX. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 160.]

January 10th, 1917.—Dr. Alfred Harker, F.R.S., President,
in the Chair.

THE following communications were read :—

1. 'On the Palæozoic Platform beneath the London Basin and Adjoining Areas, and on the Disposition of the Mesozoic Strata upon it.' By Herbert Arthur Baker, B.Sc., F.G.S. With an Appendix by Arthur Morley Davies, D.Sc., F.G.S.

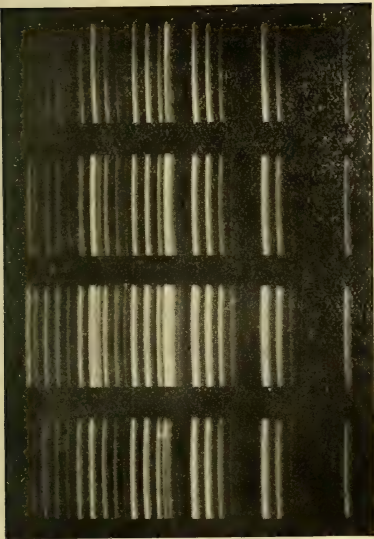
The author carries on the work of Dr. A. Strahan and Dr. Morley Davies in tracing the contours of the Palæozoic platform of the South-East of England. By comparing these with the contours of the base of the Gault, he determines the probable boundaries of the areas of the platform that were only submerged finally under the Gault sea. He analyses the effects of post-Cretaceous tilting and warping, and presents a map illustrating the contours of the Palæozoic floor at the end of the Lower Cretaceous Period.

He next discusses the successive Mesozoic overlaps on the platform, the probable areas that they respectively cover, and the relation of these to the tectonics of the platform itself. He claims that there is evidence for a second Charnian axis, parallel to that traced by Prof. P. F. Kendall, proceeding south-eastwards through Norfolk and Suffolk, east of Kent, to the North of France. He further suggests that the area between these two geo-anticlines is a geo-syncline, which, in Mesozoic times, in consequence of the accumulation of sediments within it, and the continued operation of Charnian movement, became converted into an anticline (as in the case of the Wealden area).

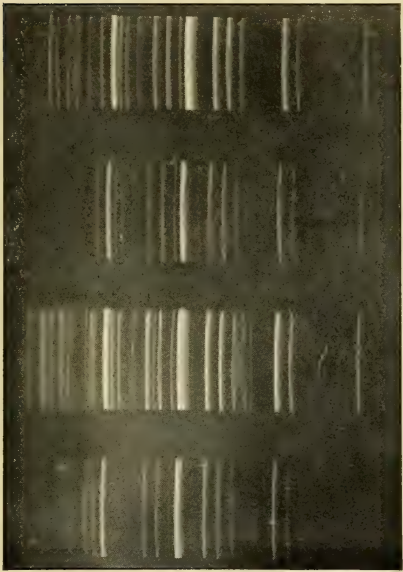
In an Appendix, Dr. Morley Davies discusses the interpretation of the Saffron-Walden boring, and its bearing on the supposed inter-Charnian trough; he also points out evidence of a post-Cretaceous Charnian anticline under London.

2. 'Balston Expedition to Peru: Report on Graptolites collected by Capt. J. A. Douglas, R.E., F.G.S.' By Charles Lapworth, LL.D., M.Sc., F.R.S., F.G.S.

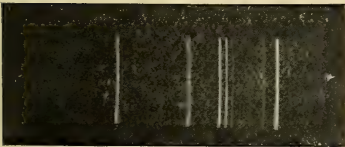
I.



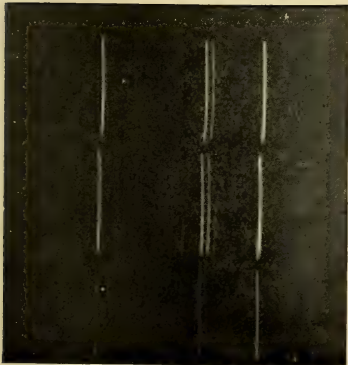
II.



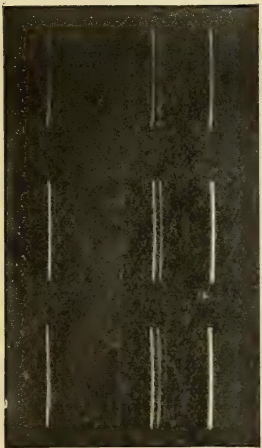
III.



V.



IV.



1.—Pressure slightly greater than $\cdot 001$ mm.
2.—Pressure slightly greater than $\cdot 001$ mm
3.—Pressure about $\cdot 001$ mm.

1 & 2.—With magnetic field at same pressure
as at 3.
3.—Without magnetic field.

Polarimeter Tube.

End of Polarimeter Tube, by reflected light only
($\times 6$ diameters). Shows detail of joining.

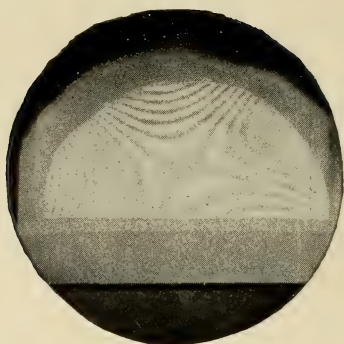


FIG. 1.

Interference-fringes formed by reflexion from a glass plate distorted by cement, and having a quartz proof-plane resting upon it. Examined by light from a mercury vacuum arc lamp.



FIG. 2.

Two disks of glass in optical contact. A diamond-cut through one does not spread to the other.

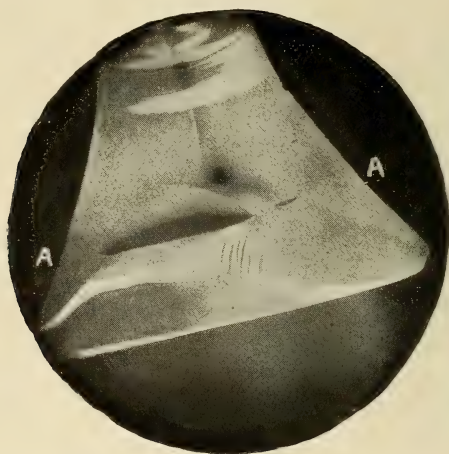


FIG. 3.

Corner broken from a cell, showing that the fracture travelled without hindrance across the joint (AA) ($\times 6$ diameters).

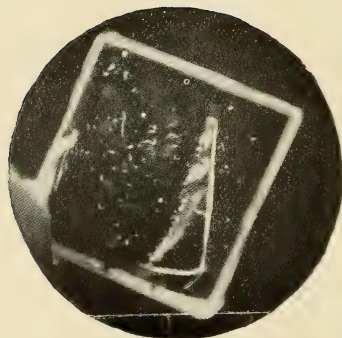


FIG. 4.

Small glass plate ($\times 6$ diameters), showing portion torn from another plate heated in optical contact with it.

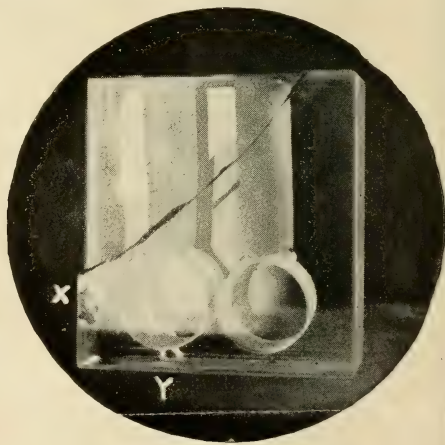


FIG. 5.

Cell after putting windows on in optical contact, heating, and then subjecting to severe mechanical strain. Windows not perfectly joined.

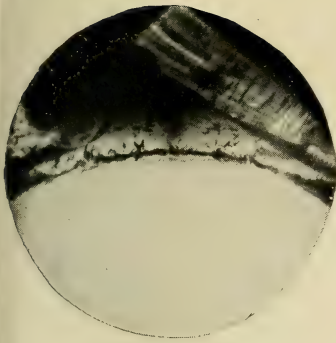


FIG. 6.

Area at X, fig. 5 ($\times 6$ diameters), to show burr.

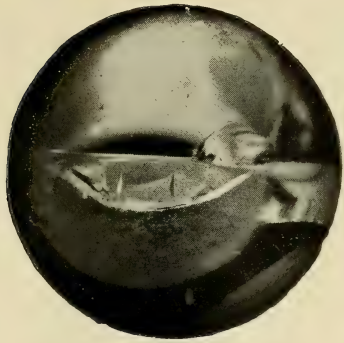


FIG. 7.

Area at Y, fig. 5 ($\times 6$ diameters). The lower edge of the fracture is guided round the drilled aperture by the burr.

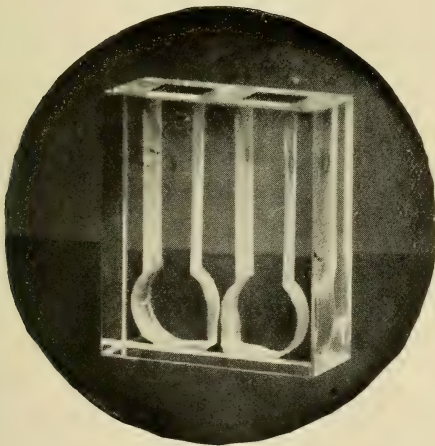


FIG. 8.

Finished cell for a Rayleigh Interference Refractometer.

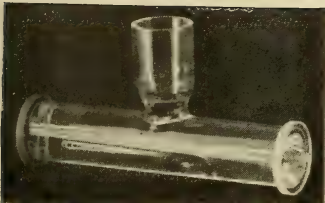


FIG. 9.

Polarimeter Tube.

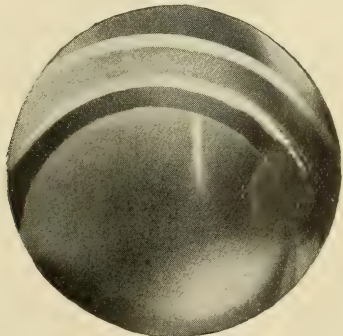
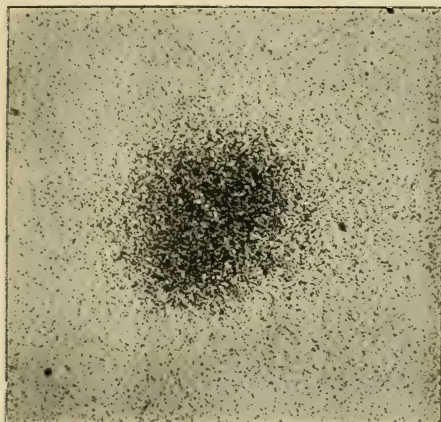


FIG. 10.

End of Polarimeter Tube, by reflected light only ($\times 6$ diameters). Shows detail of joining.



A

× 100.



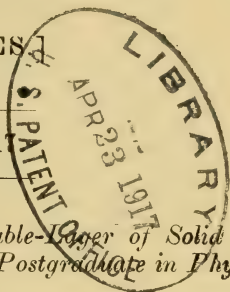
B

× 100.

THE
LONDON, EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

[SIXTH SERIES.]

APRIL 1917



XXX. *On the Surface Electric Double-Layer of Solid and Liquid Bodies.* By J. FRENKEL, Postgraduate in Physics, University of Petrograd*.

PART I.—*Intrinsic Potentials.*

§ 1. IT has been assumed by many investigators on contact electromotive forces that the latter are due to the presence of electric double-layers on the surface of metals. The existence of such layers has been conclusively proved by experiments on the thermionic and photo-electric effect. It has been shown by Richardson that the free electrons, in escaping from a heated metallic body, perform a perfectly definite amount of work at the cost of their kinetic energy due to thermal agitation. This work is measured by the constant w in Richardson's formula

$$i = A\sqrt{T}e^{-\frac{w}{kT}},$$

where i is the thermionic current, T the temperature, k the gas constant. The fact that w is always positive shows that the electric force near the surface of all metals is directed outwards (thus tending to keep the electrons back), or in other words, that the outer face of the electric double-layer is always negative, and the inner positive. The electric potential inside the metallic body must therefore exceed that of its environment by a positive quantity V , connected with

* Communicated by Prof. A. Yoffé.

w by the relation $eV=w$, where e is the electronic charge. This quantity V may be called the intrinsic potential of the body. The difference between the intrinsic potentials of two metals must be equal to their contact electromotive force (neglect being made of the Peltier effect); a fact which has been verified in a few cases by comparison of the theoretical values, obtained from thermionic data, with those directly measured by the electrostatic method. It may be mentioned here that the intrinsic potentials of different metals, as calculated from Richardson's formula, remain in rather narrow limits and amount to a few volts (4.48 volts for Tungsten)*.

It is well known that metals are not sensitive to light of any wave-length; the photo-electric emission begins when the frequency ν of the exciting light exceeds a certain critical value ν_0 , the kinetic energy of the ejected electrons $\frac{1}{2}mv^2$ being connected with ν by Einstein's formula $\frac{1}{2}mv^2=h(\nu-\nu_0)$, where h is Planck's constant. The remarkable exactitude of this formula has been conclusively proved by the recent experiments of Millikan†, who also showed that the difference between the values of $h\nu_0$ for Na and Li was just equal to their contact electromotive force (multiplied by e), as measured by the Kelvin method. In Einstein's formula $h\nu_0$ corresponds to w in that of Richardson, being equal to the energy lost by the electron on its way through the electric double-layer enveloping the metallic surface. The intrinsic potentials, calculated from the relation $Ve=h\nu_0$, are equal to 1.81 volts for Na and 2.24 volts for Li‡.

The existence of electric double-layers on the surface of metals is thus beyond doubt, and the question arises as to their origin.

§ 2. The old view, which was in favour of an external origin depending upon occluded gases, chemical action, &c., is now being supplanted by the opposite view, which, leaving to the external agencies but a secondary rôle, tends to trace the origin of intrinsic potentials to the action of *some intrinsic cause*, more appropriate for the explanation of their comparative constancy. It is the main purpose of this paper to show that such a cause really exists; its extreme simplicity is, perhaps, the only reason why it has not been noticed until now.

Let us imagine a metallic body absolutely cleaned from alien substances and placed *in vacuo*. It is composed of identical atoms packed rather closely together. Every atom

* H. Lester, Phil. Mag. March 1916.

† Phys. Rev. March 1916.

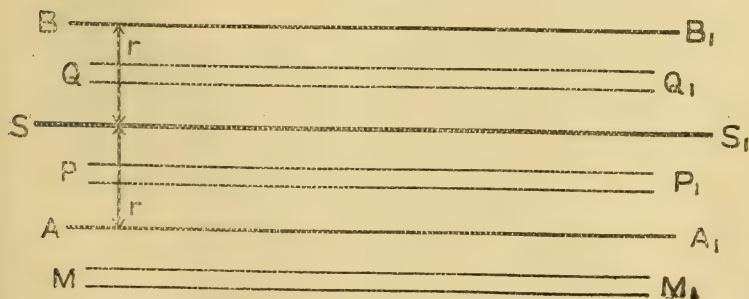
‡ The respective values of ν_0 are 43.9×10^{13} and 57×10^{13} .

consists of a positive central nucleus of minute dimensions and a cluster of electrons rotating about it. The correctness of this conception, due to Rutherford, can hardly be disputed at the present time. We may neglect the mass of the electrons compared with that of the nucleus, and therefore neglect the motion of the latter compared with that of the former. In other words, *we may consider the nuclei as immobile.*

Let us imagine a surface passing through the outermost nuclei and call it, for the sake of brevity, the surface of the body. One half of the electrons rotating around these nuclei will remain outside this surface along with a lot of other electrons belonging to nuclei which are situated within the surface at a distance from it not exceeding the radius of the largest electronic orbits. We may identify this radius, corresponding to the "valency electrons," with the atomic radius r . Thus a layer of thickness r within the surface will be positively charged owing to part of the electrons which belong to its nuclei remaining outside the surface and forming there a negative layer of the same thickness r .

This conception of an atomic electric double-layer is, as will be shown, in remarkable quantitative agreement with the experimental facts. Turning to the evaluation of the intrinsic potential, due to such a layer, we shall first assume each atom to consist (like a hydrogen atom) of a single electron at a fixed distance r from an immobile nucleus of charge $+e$, and calculate the mean electric density $\bar{\rho}_x$ at a given distance x from the surface (reckoned positive inwards), *all positions of the nuclei inside the surface and all orientations of the atoms being equally probable.*

Fig. 1.



Let SS_1 (fig. 1) represent the surface of the body (supposed plane). The planes AA_1 and BB_1 , drawn at a distance $\pm r$ from SS_1 and parallel to it, will represent the limits of positive and negative electrification respectively.

Take a very thin layer MM_1 at a distance $x > r$ from SS_1 . It contains $n dx$ nuclei per sq. cm., where dx is the thickness of the layer and n the number of atoms per c.c., with a positive charge $en dx$, which obviously must be neutralized by the electrons belonging to nuclei enclosed in two layers of thickness r on both sides of MM_1 (the part contributed by MM_1 being negligibly small).

Take another layer PP_1 of the same thickness dx at a distance $x < r$ from SS_1 . Half of the positive charge, due to the nuclei enclosed in it, is neutralized by the electrons belonging to the nuclei which are contained in a layer of thickness r on the inward side of PP_1 ; the layer on the other side of PP_1 is narrower ($x < r$) and the electrons belonging to its nuclei neutralize but a part of the other half, which can be easily calculated. In fact, take a layer of thickness $d\xi$ at distance $\xi < x$ from SS_1 ; it contains

$$n d\xi \cdot \frac{2\pi \sin \phi d\phi}{4\pi} = n d\xi \cdot \frac{\sin \phi d\phi}{2}$$

nuclei whose electrons are enclosed within PP_1 , where ϕ is the angle between the line joining the nucleus with the corresponding electron and the positive direction of x , determined by the inequality $x < r \cos \phi < x + dx$. Putting

$\cos \phi = u$, we find that $-du = \sin \phi d\phi = \frac{dx}{r}$ and

$$n d\xi \cdot \frac{\sin \phi}{2} d\phi = \frac{1}{2} n \frac{dx}{r} d\xi.$$

Integrating this from $\xi = 0$ to $\xi = x$, we find for the negative charge contributed to PP_1 by the layer PS $-\frac{1}{2} ne \frac{x}{r} dx$, whence we conclude that PP_1 contains an excess of positive charge equal to $\frac{1}{2} ne \left(1 - \frac{x}{r}\right) dx$.

Noticing that the negative charge in a layer QQ_1 on the outer side of the surface at a distance $x < 0$ from it, is contributed by the electrons belonging to a layer of thickness $r - |x| = r + x$, we find, in the same way, that it is equal to $-\frac{1}{2} ne \left(1 - \frac{|x|}{r}\right)$. Thus, for the mean volume density in different planes parallel to the surface, we get

$$\left. \begin{aligned} \rho_x &= +\frac{1}{2} en \left(1 - \frac{x}{r}\right), & 0 < x < r, \\ \rho_x &= -\frac{1}{2} en \left(1 + \frac{x}{r}\right) = -\frac{1}{2} en \left(1 - \frac{|x|}{r}\right), & -r < x < 0, \\ \rho_x &= 0, & |x| > r. \end{aligned} \right\} \quad (1)$$

We see that the distribution of electricity in the double-layer is anti-symmetrical with respect to the surface.

For the total value of the charge inside or outside the surface we easily find from (1)

$$\epsilon = \pm \frac{1}{4}ner \text{ per sq. cm.} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

We assume that the *mean* value of the electric intensity \bar{E}_x in a plane at a distance x from the surface may be derived from the equation

$$\frac{d\bar{E}_x}{dx} = 4\pi\rho_x, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

with the condition that $\bar{E}_x = 0$ for $x = -r$. This gives

$$\bar{E}_x = -\frac{\pi ne}{r} (r - |x|)^2, \quad |x| \leq r, \quad . \quad . \quad . \quad (4)$$

where $|x|$ is the absolute value of x . \bar{E}_x is always negative, *i. e.* directed outwards, and reaches its largest value $\bar{E}_0 = \pi ner = 4\pi\epsilon$ on the surface, with respect to which it is distributed anti-symmetrically. To find the distribution of potential V_x in the double-layer, we integrate the equation

$\frac{dV_x}{dx} = -\bar{E}_x$ with the condition that $V_x = 0$ for $x = -r$. We easily get from (4)

$$V_x = \frac{\pi ne}{r} \{ r^3 \pm [r^3 - (r \mp x)^3] \}, \quad . \quad . \quad . \quad (5)$$

where the upper signs refer to the case $x > 0$ and the lower to the case $x < 0$. At $x = r$, V_x reaches its maximum value which it preserves throughout the interior of the metal, forming what has been called the intrinsic potential V_r ,

$$V_r = \frac{2}{3}\pi enr^2, \quad . \quad . \quad . \quad . \quad . \quad (6)$$

of the latter.

§ 3. The deduction of (4) and (5) was based upon the approximate equation (3) $\frac{d\bar{E}_x}{dx} = 4\pi\rho_x$, the strict one being

$$\frac{\partial \bar{E}_x}{\partial x} + \frac{\partial \bar{E}_y}{\partial y} + \frac{\partial \bar{E}_z}{\partial z} = 4\pi\rho_x,$$

where E_y and E_z denote the two components of E perpendicular to the axis x , E being the real value of the electric intensity at a given point of the plane x . The lines above the differential coefficients indicate that their mean values over the whole plane should be taken. We have thus tacitly

assumed that $\frac{\partial \bar{E}_y}{\partial y} = \frac{\partial \bar{E}_z}{\partial z} = 0$ and $\frac{\partial \bar{E}_x}{\partial x} = \frac{\partial \bar{E}_x}{\partial x}$. The exact solution of the question about the error introduced by such an assumption presents great analytical difficulties, but it is clear without any calculations that this error is the smaller the more tightly the atoms are packed together,—or, in other words, the greater is the overlapping of the separate atomic fields. If the interatomic distances were large compared with the atomic dimensions, each atom would form a closed system, not interacting with the others and exerting no influence on the free electrons (if any). Thus there can be no question about the intrinsic potential of an ideal gas*. In solid and liquid bodies, where the atoms (or molecules) are very tightly packed together, the interatomic distances being of the same order of magnitude as the atomic diameters, the interatomic forces are very intense and the overlapping of the atomic fields very complete. This reduces $\frac{\partial \bar{E}_y}{\partial y}$ and $\frac{\partial \bar{E}_z}{\partial z}$ inside the double-layer to a negligible value (they are equal to zero, as well as $\frac{\partial \bar{E}_x}{\partial x}$, inside the double-layer where $\rho_x = 0$), as clearly seen from the examination of the extreme case when e tends to zero and n to infinity (the product ne remaining constant). Another important effect of the condensation of the atoms is the increase of regularity in the surface electric field, the diminution of the deflexions in the value of the intensity E , acting on the free electrons in different points of each plane, from the corresponding mean value \bar{E} .

Returning to our hydrogen-like atoms, we see that when the mean distance between them $2R = \frac{1}{\sqrt[3]{n}}$ is comparable with their diameter $2r$, the electric double-layer at the surface of the solid or liquid body is effective in producing the field \bar{E}_x (and consequently the intrinsic potential \bar{V}_r) determined by the equation $\frac{d\bar{E}_x}{dx} = 4\pi\bar{\rho}_x$, and also that this field is sufficiently regular to absorb from each escaping electron an approximately constant amount of energy equal to $e\bar{V}_r$.

* But whenever there is some interaction between the gas-molecules, there must also exist an intrinsic potential; formula (6) cannot, however, hold for a gas with any degree of accuracy.

Now every real atom may be considered, from the electrostatic point of view, as a superposition of an adequate number of such hydrogen-like atoms with a common centre containing the nuclei and with different radii corresponding to the different electronic rings. If there are κ_r electrons in the ring of radius r , they will form on the surface a double-layer of thickness $2r$ and with a charge $\epsilon_r = \pm \frac{\kappa_r}{4} enr$.

The corresponding portion of the intrinsic potential would be $V_r = \frac{2}{3} \pi e \kappa_r \cdot n \cdot r^2$, if these electrons were efficient in producing it. It can be easily shown that on account of the rapid decrease of the radius of successive rings, the portion of the intrinsic potential due to the central electrons—even in the case of such a heavy element as Hg—would be of the same order of magnitude as that due to the external (valency) electrons only. As a matter of fact, however, these central electrons—or rather the portions of the atoms corresponding to them in the above sense—are inefficient in the creation of intrinsic potential, their radii being small compared with the interatomic distances. These central portions of the atoms behave like the molecules of a gas, hardly interacting with each other and exerting no sensible influence on the free electrons (if any). We may, therefore, *replace the atoms by simplified models, consisting of the external “valency” electrons only and a corresponding positive charge at the centre.* In connexion with this it may be mentioned that such simplified models of chemical atoms have been very successfully applied by Kossel* to the explanation of the laws of chemical action, upon which the central electrons appear thus to have no effect save that of reducing the charge of the nucleus. We are now prepared to deduce on the same principles the laws of phenomena depending upon the surface electric double-layer.

Let the radius of the external ring be r , the number of electrons in it κ (κ is in general equal to the valency of the element). Then, to get the charge on either side of the metallic surface and the intrinsic potential V , we need but multiply (2) and (6) by κ . Thus

$$\epsilon = \pm \frac{\kappa}{4} enr. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

$$V = + \frac{2}{3} \pi \kappa enr^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

* Kossel, *Ann. d. Phys.* Heft iii. (1916).

simple bodies, consisting of single atoms, we immediately conclude that (1) *the intrinsic potentials of metals are always positive.*

This result corresponds to the sign + in formula (8) ; it is, as pointed out in § 1, in complete agreement with the facts.

If we suppose that the atomic radii (r) are exactly equal to half the mean interatomic distance $R = \frac{1}{2\sqrt[3]{n}}$, then, putting $r=R$ and $n = \frac{1}{8R^3}$, we may replace (8) by the following approximate formula :

$$V = + \frac{1}{4} \frac{\kappa e}{R} (10)$$

We notice that the right-hand member of this equation is of the same order of magnitude as the ionizing potential of the metal, since $\frac{1}{4} \frac{\kappa e^2}{R}$ is approximately equal to the energy required to remove one of the κ electrons to infinity : hence (2) *the intrinsic potentials of metals are of the same order of magnitude as the corresponding ionizing potentials.*

It always seemed strange to me that the units invented for the measurement of contact electromotive forces (*i. e.* the differences between the intrinsic potentials) should fit so well the ionizing potentials, which, indeed, in the case of metallic vapours amount to a few volts. On the above theory this coincidence receives a very simple and natural explanation.

Lastly, since V is proportional to κ , and since the atomic radii r are, *probably*, less variable than the valency, we see that (3) *the intrinsic potentials of metals tend to increase with their valency.*

In fact, it is well known that the alkali metals are the only ones sensitive to ordinary light : next come the divalent ones (Zn, Mg), &c. ; on the other hand, Pt ($\kappa=8$) is one of the most electronegative metals*.

A few examples are collected in the following Table (I.), the intrinsic potentials (column V.) being calculated on formula (10) ; the atomic volumes (equal to the ratio of the atomic weight A to the specific weight δ , column III.) have been used for the determination of n , by means of the relation

$$n = \frac{\delta}{A} N, \text{ where } N = 6.06 \times 10^{23} \text{ is Avogadro's number.}$$

* We shall further see (§ 6) that this is but very approximately true for pure metals unaffected by absorbed gases. For instance, potassium purified by distillation ceases to be sensitive to ordinary light.

TABLE I.—Atomic volumes and intrinsic potentials.

| I. Element. | II. Valency (κ). | III. Atomic volume. Δ/δ . | IV. $R = \frac{1}{2\sqrt[3]{n}}$ | V. Intrinsic potential (calcul.). | VI. Intrinsic potential (observed). | VII. Ionizing potential. |
|----------------|---------------------------------|--|-------------------------------------|--|--|--------------------------------|
| Na | 1 | 23.7^{-1} cm. | 1.6×10^{-8} cm. | 1.7 volts. | 1.81 | |
| Li | 1 | 11.9 | 1.27×10^{-8} | 2.14 | 2.21 | |
| Hg | 2 | 14.8 | 1.4×10^{-8} | 4.2 | ... | 4.9 |
| Zn | 2 | 9.5 | 1.25×10^{-8} | 5.2 | 3.1 | 3.96 |
| Al | 3 | 10.4 | 1.21×10^{-8} | 6.7 | | |
| Pb | 4 | 18.3 | 1.46×10^{-8} | 7.4 | | |

It will be seen that the calculated values of V for Na and Li are in excellent agreement with Millikan's values (§ 1)*. As to the other values (except that for Hg, which also seems of the correct magnitude), they are obviously too high, and increase too rapidly with κ . This circumstance is easily explained by the fact that r is, in general, *less* than R and that the ratio $\frac{r}{R}$ decreases as κ increases. In fact, the interference between the external electronic rings of neighbouring atoms must, obviously, increase with the number (κ) of electrons in these rings; their diameters must, therefore, contract compared with the interatomic distances—or rather conversely—the distances between the atoms must increase, compared with their diameters, as the valency κ increases.

How far these considerations correspond to the facts will be seen from the next Table (II.), in which the atomic radii are calculated by means of the strict equation (8) from the known values of the intrinsic potentials, as derived directly from the thermionic effect†. It must be emphasized that these values, obtained at very high temperatures after an almost complete expulsion of occluded gases, are really characteristic of the metal itself, and are, consequently, much more reliable than those derived from the photo-electric effect.

* This close agreement is, probably, merely accidental, because (1) Millikan's values do not relate to pure Na or Li, *i. e.* free from absorbed gases, (2) r cannot be exactly equal to R. The coincidence of the *ratios*, theoretical and experimental, is, however, very significant.

† H. Lester, Phil. Mag. March 1916, and Baedeker, *Elektr. Erscheinungen in metallischen Leitern* (1911).

TABLE II.—Intrinsic potentials and Atomic radii.

| I. Element. | II. Valency κ . | III. Atomic weight A. | IV. Specific weight δ . | V. Intrinsic potential (observed). | VI. Atomic radius r (calculated). | VII. $\frac{1}{2}$ inter- atomic distance R. | VIII. $\frac{r}{R}$. |
|----------------|------------------------------|--------------------------------|---|---|--|---|--------------------------|
| C..... | 4 | 12 | 1.80 | 4.55 volts. | 0.65×10^{-8} | 1.05×10^{-8} | 0.63 |
| Ta | 5 | 181 | 16.6 | 4.51 | 0.74×10^{-8} | 1.24×10^{-8} | 0.60 |
| Mo | 6 | 96 | 9.0 | 4.59 | 0.67×10^{-8} | 1.21×10^{-8} | 0.55 |
| W | 6 | 184 | 19.1 | 4.48 | 0.61×10^{-8} | 1.18×10^{-8} | 0.52 |
| Os | 8 | 191 | 22.5 | 4.7 | 0.52×10^{-8} | 1.13×10^{-8} | 0.46 |
| Pt | 8 | 195 | 21.4 | 5.1 | 0.57×10^{-8} | 1.16×10^{-8} | 0.49 |

The values of r in column VI. are of the right magnitude and decrease with κ , with the exception of that for carbon, which is too small; this does not, however, affect the ratios $\frac{r}{R}$ (column VIII.), which regularly decrease as κ increases, being approximately equal to $\frac{1}{2}$. The values of V, calculated on the assumption $r=R$ (as in Table I.), would have been thus about four times larger than the observed ones.

We have hitherto taken no account of the effect of the partial ionization of the metallic atoms, revealed by the presence of free electrons. This effect may be just as well negative as positive, depending possibly on the temperature. It is clear, however, that it may be considerable only when κ is small (in the case of mono- and di-valent atoms). But as the ionization depends upon the intensity of the inter-atomic forces (as proved by the fact that it disappears in metallic vapours) it may be much less for the superficial atoms, exposed to such forces from one side only, than for the internal ones. Whatever it may be, the results of this theory, which are equally applicable both to metals and dielectrics, seem to support the view that the ionization has no sensible effect upon the surface layer (see below).

§ 5. Let us imagine an equipotential surface, enclosing as tightly as possible that of the metal, without, however, penetrating into the double-layer, and call its potential ϕ , the external potential of the metal. If there were no double-layer, ϕ would be equal to the potential of the internal points. The action of the double-layer consists in increasing the latter by a fixed value V , and we shall call the sum $\phi + V$ the internal potential of the body. }

Let us take two metals A and B whose external potentials are zero, the intrinsic ones being equal to V_A and V_B respectively, and put them in contact with each other, so that their surface electric double-layers partly overlap, the negative half of the one coinciding with the positive half of the other. The electric field in the residual double-layer will be directed from A to B if $V_A > V_B$, and will drive from B to A a number of electrons sufficient for its annihilation, *i. e.* for the equalization of the internal potential in the system AB. Denoting by ϕ_A and ϕ_B the variations of the internal potential of A and B respectively, we see that they will be equal to the external potentials of the metals in the final state and will be connected by the equation

$$V_A + \phi_A = V_B + \phi_B.$$

We shall thus observe an external electric field, due to a positive charge on B ($\phi_B > 0$) and a negative charge on A ($\phi_A < 0$), corresponding to a potential difference

$$\phi_B - \phi_A = V_A - V_B,$$

as if the latter really existed between the metals. As a matter of fact, however, their internal potentials are the same and will remain equal after their separation. Measuring their mutual attraction we shall obtain the external potential difference, which is equal and opposite to the difference of the intrinsic potentials. If A and B were connected with two other bodies C_A and C_B of the same material characterized by the intrinsic potential V_C , then the internal potentials of these bodies being equal to the common internal potential of A and B, the external potentials ϕ_{AC} and ϕ_{BC} must be equal too. There will be, consequently, no electric field between C_A and C_B , and if the latter are the quadrants of an electrometer, there will be no deflexion when A and B are disconnected. But if the surrounding gaseous medium is ionized, the surface charge of A and B, acquired during the contact, will be dissipated; the external potential difference between them will disappear, while the internal one will resume its initial value $V_A - V_B$, equal, of course, to the difference between the external potentials of C_A and C_B , which will be measured by the deflexion of the needle. This is the principle of the ionization method for the determination of contact electromotive forces. It will be noticed that the electrometer always measures the internal potential difference of the metals considered.

At ordinary temperatures but very few electrons can

escape from the metal. As to the external electrons or negative ions (if any), they will be dragged into the double-layer each time that they sufficiently approach it, and, sticking in the positive side, may diminish the potential fall at the surface. But neutral molecules may also stick near or in the double-layer, and form additional double-layers of the same or opposite sign. In those cases when the formation of such extra double-layers is effected at the cost of the potential energy of the primitive double-layer, the adsorbed molecules must diminish the intrinsic potential of the metal in proportion to its original value (but not, of course, beyond zero). This appears to be in full agreement with the recent experiments on contact electromotive forces *, and explains their dependence on minute quantities of occluded (or rather adsorbed) gases.

It is clear that the contact electromotive forces, due to the presence of surface electric double-layers, have nothing to do with the thermo-electric forces generated by the difference in the concentration and, consequently, the partial pressure of the *free* electrons in adjoining layers. The Peltier heat depends upon their kinetic energy and not upon the energy of the rotating *bound* electrons forming the atomic double-layer.

In conclusion a few words must be said about the electrification of insulators and electrolytes.

Insulators are distinguished from conductors by the absence of free electrons and not by the absence of intrinsic potentials, which in this case may be positive as well as negative, depending upon the structure of the molecules. A mere contact between two dielectrics is insufficient for their electrification, which will take place as soon as free electrons are liberated near the contact surface. The old means of doing this is *friction*. Indeed, the electrification of bodies by friction was the first experimental fact discovered in the phenomena of electricity. The exceedingly high potentials reached in this way are simply explained by the fact that the electric charges remain concentrated in those places only where they have been formed (instead of being distributed over the whole surface, as in the case of conductors), and may be very large, thanks to the large capacity of the condenser formed by the adjacent surfaces; this capacity enormously decreases when the bodies are torn apart, causing a corresponding increase of the potential difference, which may be initially equal to the contact electromotive force, that is, to the difference of intrinsic potentials of the bodies.

* See, for instance, Shaw, *Phil. Mag.* vol. xxv. pp. 255-256 (1913).

A more modern and efficient method of liberating free electrons would consist in the ionization of the layers adjacent to the contact surface by means of Röntgen rays. According to this theory, the free electrons would be driven by the electric field in the residual double-layer from the body with the smaller intrinsic potential to that with the larger, until the electromotive force is completely annihilated owing to the formation of the condenser above referred to. One of the dielectrics may be, of course, replaced by a metal. I am not, however, aware of any experiments having been made in this direction.

The electrolytes, again, differ from the metals not by the absence of intrinsic potentials, but by the absence of free electrons which are replaced by ions. These ions cannot penetrate in the metal, but must form electric double-layers near its surface, along with the ions of the metal itself. A complete equalization of internal potentials seems, however, impossible in this case, since besides the mere electrostatic forces there are other forces—especially the osmotic pressure of the ions—which now come into play.

PART II.—*Surface Tension.*

§ 6. When mercury is in contact with an electrolyte, its surface-tension is diminished, as compared with its value *in vacuo*, by about one-third of the latter. This value may be restored by the application of an external electromotive force, balancing the contact potential difference, and is again diminished when the balance is destroyed. The phenomena of electro-capillarity disclose, thus, an intimate relation between the contact electromotive forces and surface-tension. On this theory, both are due to the same cause—the atomic (or molecular) electric layer enveloping the surface of solid and liquid bodies—the former depending upon its intrinsic potential, and the latter upon its energy.

That a certain portion of the surface-tension must be due to this energy immediately follows from the fact that the latter is proportional to the surface of the body. The considerable effect produced upon the surface-tension of mercury by the secondary electric layers which are formed when it is in contact with an electrolyte, shows that this portion may be very large. In order to make an estimate of it, we shall compare the surface-tension σ , numerically equal to the (free) energy of unit surface of the liquid, with the electrostatic energy W , enclosed per sq. cm. in its surface electric layer. Let us, as before, begin with metals.

The mean electric intensity in the double-layer of a κ -valent metal at distance x from the surface is given by the equation

$$\overline{E}_x = -\frac{\pi\kappa en}{r}(r-|x|)^2, \quad |x| < r, \quad . \quad . \quad . \quad (11)$$

which is derived from the multiplication of (4), § 2, by κ .

From this W may be calculated by means of the relation

$$W = \frac{1}{8\pi} \int_{-r}^{+r} \overline{E}_x^2 dx = \frac{1}{4\pi} \int_0^r \overline{E}_x^2 dx,$$

which gives

$$W = \frac{\pi}{20} (\kappa en)^2 r^3, \quad . \quad . \quad . \quad (12)$$

or, by (7) and (8), $W = \frac{3}{10} V\epsilon$ (it will be noticed that $V\epsilon$ is the energy of the "equivalent" double-layer). Putting $\epsilon = \frac{3}{8\pi} \frac{V}{r}$, we may replace (12) by the following formula :

$$W = \frac{9}{80\pi} \frac{V^2}{r}, \quad . \quad . \quad . \quad (13)$$

which is very convenient for the calculation of W when the intrinsic potential V and the atomic radius r are known. We have seen that for mercury $r = R = 1.4 \times 10^{-8}$ cm. and $V = 4.2$ volts, or $\frac{4.2}{300}$ C.G.S.E. units (Table I.). Consequently

$$W = \frac{9(4.2)^2}{80\pi(300)^2 1.4 \times 10^{-8}} = 472 \frac{\text{erg.}}{\text{cm.}^2},$$

which corresponds to a surface-tension of $472 \frac{\text{dyn.}}{\text{cm.}}$. As a matter of fact, the surface-tension of mercury is $436 \frac{\text{dyn.}}{\text{cm.}}$

(according to some other measurements even 460). We see that W is slightly *larger* than σ . This is simply explained by the fact that r is not equal to, but slightly less than, R . The surface-tension of mercury may be thus *wholly* accounted for by the electrostatic energy of its surface double-layer. There remains, apparently, no room for the hypothetical cohesive forces upon which the classical theories of Laplace and Gauss were based. We shall assume that in the case of *all* liquid bodies these forces have no direct influence upon the surface-tension, and that the latter depends *exclusively* upon the energy of their electric double-layers; expressing this mathematically, we get

$$\sigma = W. \quad . \quad . \quad . \quad (14)$$

Taking the experimental values of the surface-tension of fused metals *, I have calculated, by means of (14) and (12), their atomic radii (r), and further, by means of (8), the corresponding intrinsic potentials (V). The results are collected in the following Table (III.). The numbers (κ), tabulated in the second column, do not, strictly speaking, represent the valency, but the probable number of external electrons, determined by the position of the corresponding metal in the periodic system. As a matter of fact, this number may be different. For instance, copper, silver, and gold are included in the first group, although copper is often di-valent, and gold tri-valent. It is possible that for silver κ is also larger than 1.

TABLE III.—Surface-tension and intrinsic potentials.

| I. Element. | II. Valency κ . | III. Atomic weight A. | IV. Specific weight δ . | V. Surface- tension σ dyn. cm. (observed). | VI. Atomic radius (calcul.) $r \times 10^8$ cm. | VII. Intrinsic potential (calcul.) V volts. | VIII. Intrinsic potential (observed) volts. |
|----------------|------------------------------|--------------------------------|---|--|---|---|---|
| Na | 1 | 23 | 0.93 | 294 | 2.4 | 4.2 | 1.81 |
| K | 1 | 39 | 0.83 | 415 | 2.58 | 2.55 | — |
| Ag | 1 | 108 | 9.51 | 784 | 1.97 | 6.23 | — |
| Zn | 2 | 65 | 6.48 | 104(?) | 0.58 | 1.24 | — |
| Cd | 2 | 112 | 8 | 815(?) | 1.43 | 5.42 | — |
| Hg | 2 | 201 | 13.6 | 436 | 1.36 | 4.00 | — |
| Sn | 4 | 119 | 6.94 | 681 | 0.99 | 4.21 | — |
| Pb | 4 | 207 | 10.64 | 536 | 0.99 | 3.66 | — |
| Sb | 5 | 120 | 6.5 | 317 | 0.68 | 2.30 | — |
| Bi | 5 | 208 | 10.0 | 460 | 0.83 | 3.11 | — |
| Fe | 8 | 56 | 6.88 | 950 | 0.42 | 3.18 | — |
| Pt | 8 | 195 | 21.3 | 1820 | 0.57 | 5.10 | 5.1 |

Let us first consider the calculated values of the intrinsic potentials (column VII.). The main fact about them is that *they are all of the right order of magnitude and lie in very narrow limits*, in spite of the considerable variation of κ . The only metal for which the direct comparison of the

* Landolt-Börnstein, *Physikalisch-Chemische Tabellen* for 1911, p. 114. It must be remarked that the discrepancy between the values of σ found by different persons does not affect the order of magnitude.

theory with experiment may really be effected, is Pt, and it happens that the calculated value of V *exactly* agrees with that derived *under nearly the same conditions* from the thermionic effect*. In fact, the latter has been measured for very high temperatures, as well as the surface-tension of fused platinum, after an almost complete expulsion of occluded gases, and is really characteristic of pure platinum. This cannot be said about Na, no care having been taken in Millikan's experiments to get rid of occluded gases. There are strong indications to the effect that the latter greatly diminish the intrinsic potential of the alkali metals†, and it is very probable that the calculated value of V (4.2 volts) for *pure* Na is nearer to the truth than Millikan's value.

The exceedingly high fusion-point of the other elements in Table II. has not allowed hitherto of a determination of their surface-tension. Their intrinsic potentials, however, are very close to those calculated in Table III., so that at first sight it may seem that both are got from the same source.

Further, the value of V for cadmium seems too high and that for Zn too low. This may perhaps be due to a corresponding error in the experimental values of σ ; it is, indeed, very strange that the surface-tension of metals so closely akin as zinc and cadmium should be so widely different. Whatever it may be, the Table correctly expresses the fact that Zn is, under ordinary conditions, one of the most electro-positive metals, highly photo-electric, and positively electrified when put in contact with all the other metals except the alkali ones. More than that, if we arrange the elements of Table III. (except Na, K, and Cd) in the order of increasing intrinsic potentials, we get the following series :

(+) Zn, Sb, Bi, Fe, Pb, Hg, Sn, Pt, Ag (-),

every member of which should be positively electrified when put in contact with one of the next. This series (corresponding to the "Volta series") is not very different from those which were experimentally found. For instance, Volta found : (+) Zn, Pb, Sn, Fe, Ag (-) ; Seebeck : (+) Zn, Pb, Sn, Sb, Bi, Fe, Pt, Ag (-) ; Auerbach : (+) Zn, Sn, Pb, Sb, Bi, Hg, Fe, Ag, Pt (-).

Lastly, the theoretical values of the contact electromotive forces, equal to the difference between the calculated

* See Table II., § 4.

† The repeated distillation of potassium in a very high vacuum caused its photo-electric effect to disappear completely. See Hughes, *Phil. Mag.* vol. xxviii. p. 338 (1914). Also Wiedemann & Hallwachs, *Verh. d. Deutsch. Phys. Ges.* p. 107 (1914).

intrinsic potentials, are of the right order of magnitude (about 1 volt).

Thus, the agreement of the theory with the facts is, on the whole, very satisfactory.

§ 7. Let us now turn to the atomic radii (column VI. of Table II.). The main fact is, again, the right order of magnitude of all the values found for different atoms. Another striking fact is that the atomic radii regularly decrease as the valency increases. This result was anticipated in § 4. It was pointed out there that, "as the interference between the rings of neighbouring atoms increases with the number of electrons in them, the ratio of their radius to their mutual distance must decrease," and it was thought possible to explain by this circumstance the too high values obtained for the intrinsic potentials of Zn, Al, and Pb, on the assumption that r , the atomic radius, was equal to $R = \frac{1}{2\sqrt[3]{n}}$, where $2R$ is the mean interatomic

distance. (This assumption would give for the intrinsic potential of Pt a value about five times as large as that calculated from the surface-tension.) The quantitative examination of this question from the point of view of Bohr's theory of atomic dynamics leads to the same result.

If κ equidistant electrons of charge $-e$ and mass m rotate with an angular velocity ω in a circle of radius r with an immobile nucleus of charge κe at the centre, the condition of equilibrium between the attraction to the centre and the centrifugal force is expressed by the equation

$$(\kappa - s_\kappa) \frac{e^2}{r^2} = m\omega^2 r, \quad . \quad . \quad . \quad . \quad (A)$$

where $s_\kappa = \frac{1}{4} \sum_{i=1}^{\kappa-1} \operatorname{cosec} \frac{i\pi}{\kappa}$, and the term $-\frac{s_\kappa e^2}{r^2}$ corresponds to the mutual repulsion of the electrons. According to Bohr*, this motion is stationary (unaffected by radiation) then only, when the angular momentum of each electron is an integral multiple of $\frac{h}{2\pi}$, where h is Planck's constant, that is when

$$mr^2\omega = i \frac{h}{2\pi}. \quad (i=1, 2, 3, \dots). \quad . \quad . \quad . \quad (B)$$

From (A) and (B) we get for the possible values of r ,

$$r_i = \frac{ai^2}{\kappa - s_\kappa}, \quad a = \frac{h^2}{4\pi^2 e^2 m} = 0.55 \times 10^{-8}, \quad (i=1, 2, 3, \dots) \quad (15)$$

* Phil. Mag. vol. xxvi. pp. 1 & 476 (1913).

where a is equal to the radius of the first stationary circular orbit for hydrogen ($\kappa=1$). If the influence of internal electronic rings on the external one is reduced to a simple diminution of the effective central charge, as was assumed throughout this work, then formula (15) determines the possible radii of an atom whose valency is equal to κ . It is at once clear from this formula that *the atomic radii must decrease with the valency, provided i is the same for different atoms.*

As we shall see, this condition seems to be satisfied in the case of many metals in the solid or liquid state, the atomic radii being determined by the universal condition

$$i=2, \quad . \quad , \quad . \quad . \quad . \quad . \quad (16)$$

in conjunction with (15).

In the following Table (IV.), some of the values of r , calculated from the surface-tension and taken from Table II., are compared with the values r_2 , calculated on Bohr's theory by means of (15) and (16) on the one hand, and with half the inter-atomic distances R on the other. The values of s_κ are given in column III.

TABLE IV.—Atomic radii and Bohr's theory.

| I. Element. | II. Valency κ . | III. s_κ . | IV. $\frac{1}{2}$ inter- atomic distance $R \times 10^3$. | V. Atomic radius (calc. from σ or V) $r \times 10^3$. | VI. Atomic radius (calc. on Bohr's theory) $r_2 \times 10^3$. | VII. r/r_2 . |
|----------------|------------------------------|----------------------|--|---|--|-------------------|
| K | 1 | 0 | 2.00 | 2.58 | 2.2 | 1.15 |
| Hg | 2 | 0.25 | 1.40 | 1.36 | 1.26 | 1.08 |
| C | 4 | 0.96 | 1.05 | 0.65* | 0.73 | 0.9 |
| Pb | 4 | 0.96 | 1.49 | 0.99 | 0.73 | 1.35 |
| Sb | 5 | 1.38 | 1.46 | 0.68 | 0.61 | 1.11 |
| Ta | 5 | 1.38 | 1.27 | 0.74* | 0.61 | 1.21 |
| W | 6 | 1.83 | 1.18 | 0.61* | 0.53 | 1.15 |
| Fe | 8 | 2.81 | 1.11 | 0.42 | 0.43 | 0.98 |

* These values are calculated from the thermionic effect; all the others are calculated from the surface-tension.

The parallelism between the values in columns V. and VI. is obvious, although the former are somewhat larger than the latter.

It would be of course unreasonable to expect a complete coincidence between them, since the equations (A) and (B) were deduced for an isolated atom, subject to no external forces, while such forces are very intense in a solid or liquid body. We should expect the conditions underlying these equations to be realized when the metal is vaporized and the interaction between its atoms becomes feeble. In fact, experiments on the single-line spectra, excited by slow cathode rays in the vapours of Hg, Zn, Cd, and other metals of the same group, indicate that the frequency and energy of the light emitted corresponds to the transition of one of the electrons from the fourth stationary orbit on the third one * ($i=3$). The radius of this third orbit

$$r_3 = \frac{9a}{2-0.25} = 2.83 \times 10^{-8} \text{ cm. (see p. 312),}$$

is, thus, the normal atomic radius of the di-valent metals in the gaseous state. When the metal is condensed, these orbits must contract, being too large compared with the inter-atomic distances, and the electrons are forced to remain on the second stationary orbits with a radius

$$r_2 = \frac{4}{9} r_3 = 1.26 \times 10^{-8} \text{ cm.}$$

This tendency of the external electrons towards stationary orbits of higher order (second, third) seems to constitute a general, fundamental property of the metallic atoms, distinguishing them from the atoms of dielectrics, which, under ordinary conditions, keep their external electrons on the first stationary orbit (corresponding to $i=1$).

As the work required to remove an electron from its orbit, *i. e.* to ionize the atom, is inversely proportional to the radius, we see at once that the ionizing potentials of metals although increasing with the valency, must be much smaller than those of the dielectrics, a conclusion which is fully

* Franck & Hertz, *Verh. d. D. Phys. Ges.* xv. p. 34 (1913); McLennan (and others), *Proc. Roy. Soc.* v. 92, Oct. 1916.—The frequency is represented by the formula $\nu = \left(\frac{3}{2}, S\right) - \left(\frac{4}{2}, P\right)$, or approximately $\nu = 4\kappa \left(\frac{1}{3^2} - \frac{1}{4^2}\right)$, where κ is Rydberg's constant. This corresponds to the energy $h\nu$, acquired by an electron moving through a potential fall of $300 \frac{h\nu}{e} \simeq 4$ volts, or (approximately), to the energy necessary to remove the electron from the third orbit, as can be calculated by means of formula (15), taking $\kappa=2$ and $i=3$.

confirmed by experiment*. Further, the ionization of metals in the solid or liquid state must be much larger than that of the dielectrics under the same conditions, which accounts for the presence of free electrons in the former and their absence in the latter.

Lastly, the surface-tension of metals must be much larger than that of dielectrics, since, other things equal, it is proportional to the cube of the atomic radius. This conclusion is in a striking agreement with the facts†. The surface-tension of dielectrics does not, indeed, exceed a few tens, while that of the metals, as shown above, is measured by hundreds and even thousands of dynes per cm. The salts (fused) occupy in this respect an intermediate position.

A few examples, taken from Freundlich's *Kapillarchemie*, are collected in the following Table (V.), illustrating the above law.

TABLE V.—Surface-tension of dielectrics.

| Substances. | Temperature (centigr.). | Surface-tension. |
|---------------------------------------|----------------------------|------------------|
| H ₂ | −259° | 2 |
| N ₂ | −195·9 | 8·3 |
| O ₂ | −182·7 | 13 |
| A | −186·1 | 11 |
| Cl ₂ | − 72 | 33·6 |
| Sulphur..... | +160 | 60 |
| CO ₂ | + 15·2 | 1·8 |
| SO ₃ | + 20 | 30 |
| Paraffin | + 54 | 30 |
| Benzene | + 20 | 28·8 |
| Acetone | + 20 | 23 |
| Chloroform | + 20 | 26 |
| NaCl | 820 | 120 |
| KCl | 790 | 100 |
| Na ₂ CO ₃ | 850 | 213 |
| K ₂ CO ₃ | 880 | 170 |

Argon is mono-atomic, as Fe and Pt, and has the same number of electrons in the external ring (8), while its surface-tension is about 100 times smaller than that of the other two elements. On our theory this is simply explained

* The ionizing potential of Zn, Cd, Mg, Hg, is 3·96, 3·74, 4·28, 4·9 volts respectively; that of helium is 20·5 volts, of neon 16·0, of argon 12, hydrogen 10 volts.

† Strictly speaking, it refers only to mono-atomic substances; but, as will be shown later, the combination of atoms in molecules usually tends to diminish the surface-tension.

by the fact that the radius of an A atom is about $\sqrt[3]{100}=4.6$ times smaller than that of Fe or Pt, *i. e.* is equal to the radius of the first stationary orbit*. This circumstance also accounts for its chemical inactivity.

To show how far our theory is applicable to compound substances, we shall take the simplest one, liquefied hydrogen, and calculate its surface-tension, assuming for the molecule H_2 the model so successfully applied by Debye† to the calculation of the dispersion of light in hydrogen gas.

Debye's model consists, as well known, of two hydrogen nuclei at a fixed distance b from each other, and two electrons, situated in two opposite points of a circle whose centre lies at the middle of the line joining the nuclei and whose plane is perpendicular to the said line, the radius of the circle being a , and the angular velocity of the electrons ω .

The condition of equilibrium for the nuclei is

$$\frac{e^2}{(2b)^2} = \frac{2e^2b}{(a^2+b^2)^{3/2}}, \text{ or } (1+9^2)^{\frac{3}{2}}=8, \text{ whence } 9=\frac{a}{b}=\sqrt{3}, \quad (A)$$

and for the electrons

$$\frac{2e^2 \cdot a}{(a^2+b^2)^{3/2}} = \frac{e^2}{(2a)^2} = m\omega^2 a, \text{ whence by means of (A),}$$

$$\frac{ma^3\omega^2}{e^2} = \frac{3\sqrt{3}-1}{4}. \quad \dots \quad (B)$$

To this Debye adds the "quantum condition" that the angular momentum of each electron should be equal to $1 \cdot \frac{h}{2\pi}$

$$m\omega a^2 = \frac{h}{2\pi}. \quad \dots \quad (C)$$

The solution of (B) and (C) gives $a=0.67 \times 10^{-8}$ and $b=0.46 \times 10^{-8}$.

According to the general principle outlined in the end of § 3, we shall obtain the whole electric field in the quadruple layer on the surface of hydrogen (liquid) by a simple addition of the fields due to the separate constituents of the H_2 molecule, considering it as a superposition of two pairs of doublets the free ends of which are formed by the nuclei and the electrons, the opposite ends being fixed at the centre.

* The exact calculation gives for argon ($A=40$, $\delta=1.42$, $\kappa=8$), $r=0.22 \times 10^{-8}$ cm.

† *Ber. Bayer. Akad.* p. 1 (1915).

According to (11), the electric intensity due to the nuclear doublets is equal to

$$\bar{E}_{H,x} = + \frac{2\pi en}{b} (b - |x|)^2, \quad . \quad . \quad . \quad (D)$$

and that due to the electronic doublets,

$$\bar{E}_{e,x} = - \frac{2\pi en}{a} (a - |x|)^2, \quad . \quad . \quad . \quad (E)$$

the whole intensity \bar{E}_x being equal to the sum of $\bar{E}_{H,x}$ and $\bar{E}_{e,x}$ for $|x| < b < a$, and to $\bar{E}_{e,x}$ for $|x| > b$ (*i. e.* outside the double-layer corresponding to the nuclei). For the energy W per sq. cm. we get

$$\begin{aligned} W &= \frac{1}{8\pi} \int_{-a}^{+a} \bar{E}_x^2 dx = \frac{1}{4\pi} \int_0^a \bar{E}_x^2 dx \\ &= \frac{1}{4\pi} \int_0^a \bar{E}_{e,x}^2 dx + \frac{1}{4\pi} \int_0^b \bar{E}_{H,x}^2 dx - \frac{1}{2\pi} \int_0^b \bar{E}_{e,x} \bar{E}_{H,x} dx. \end{aligned}$$

Taking for n (the number of molecules per c.c.)

$$n = 6.06 \times 10^{23} \frac{\delta}{M},$$

where δ is the specific weight of liquid hydrogen and M its molecular weight ($\delta = 0.075$, $M = 2$) and performing the calculations, we find

$$W_e = \frac{1}{4\pi} \int_0^a \bar{E}_{e,x}^2 dx = 21, \quad W_H = \frac{1}{4\pi} \int_0^b \bar{E}_{H,x}^2 dx = 7,$$

and

$$W_{e,H} = \frac{1}{2\pi} \int_0^b \bar{E}_{e,x} \bar{E}_{H,x} dx = 24,$$

whence $W = W_e + W_H - W_{e,H} = 4$, which is very near to the experimental value of the surface-tension of liquid hydrogen $\sigma = 2$ (see Table V.).

When the structure of the molecule is known, the calculation of the surface-tension presents a very simple problem, and I shall not, therefore, dwell upon it any longer. The essential feature in this case is *the participation of the positive nuclei in the creation of the surface electric field, causing a diminution of its energy*. This is why the surface-tension of salts is always less than that of the corresponding metals, and the surface-tension of dielectrics of *any* composition less than that of the salts.

In conclusion, it may be mentioned that our theory gives the right dependence of the surface-tension upon the density

and, consequently, the temperature (for a given substance), since $\sigma = W$ is proportional to n^2 , that is, to the square of the density δ . In this, however, it does not differ from the older theories.

§ 8. The fact that the energy of the surface electric double-layer is sufficient to account for the surface-tension, indicates that the latter does not directly depend upon cohesive forces. The existence of these forces becomes, however, manifest, when instead of the energy and the corresponding tension parallel to the surface we consider the *stress* perpendicular to the surface and measured by the attraction between the two halves of the double-layer. The existence of an ordinary condenser implies that the attraction between the oppositely charged surfaces which form it is balanced by some external forces, and the same, *mutatis mutandis*, may be said about the molecular double-layer. In the outer half the attraction of the charges is balanced by the centrifugal force due to their rotation. The centres of the atoms or molecules contained in the other half are attracted outwards, and the fact that, nevertheless, they remain in equilibrium (statistical) implies the existence of cohesive forces pulling them in the opposite direction. In the absence of heat-motion, *i. e.* at absolute zero, the resultant of these cohesive forces P , reckoned per unit surface of the double-layer, must be equal to the corresponding electric stress F . To calculate F we have to integrate over one-half of the double-layer the product of the electric density $\bar{\rho}_x$ and the electric intensity \bar{E}_x , which in the case of a simple body of valency κ gives on account of (1) and (4), § 3,

$$F = \int_0^r \bar{\rho}_x \bar{E}_x dx = \frac{\pi}{8} (\kappa en)^2 \cdot r^2. \quad . \quad . \quad (17)$$

Comparing this with the expression (12) for the energy W , we get

$$F = \frac{5}{2} \frac{W}{r} \frac{\text{dynes}}{\text{cm.}^2}. \quad . \quad . \quad . \quad (18)$$

Thus, *the whole volume of the body is in a state of stress*, measured by F . Taking for $W = \sigma$ $100 \frac{\text{dyn.}}{\text{cm.}}$, for $r 10^{-8}$ cm., we get $F = 2.5 \times 10^{10} \frac{\text{dyn.}}{\text{cm.}^2}$, or about 25,000 kilograms per sq. cm. This is of the same order of magnitude as the internal pressure of liquids at ordinary temperatures. If, neglecting the influence of the heat-motion at these temper-

atures, we write the condition of equilibrium in the same form

$$P = F, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

and identify P with the internal pressure of the liquid, we get the following relation between surface-tension $\sigma = W$ and internal pressure

$$P = \frac{5}{2} \frac{\sigma}{r}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

Although this relation should strictly hold only for a simple substance, we may, however, expect that, applied to compound ones, it should yield for r —the mean radius of the molecule—a value of the right order of magnitude. In fact, we have for ether, alcohol, and water, $\sigma = 19.7, 25.8, 77.0 \frac{\text{dyn.}}{\text{cm.}}$, and $P = 1400, 2200, 10,700 \frac{\text{kg.}}{\text{cm.}^2}$ respectively; the corresponding values of r , calculated by means of (20), are $3.6 \times 10^{-8}, 3 \times 10^{-8}$, and $1.7 \times 10^{-8} \text{ cm.}$ Unfortunately, P has been determined for very few substances. It would be very desirable to calculate the internal pressure of liquid metals from their vaporization heat (by means of Stefan's formula

$$(P - p)v = Q,$$

where Q is the latent heat of vaporization, v the specific volume, p the vapour pressure).

According to our theory, P must be equal to $28,000 \frac{\text{kg.}}{\text{cm.}^2}$ for Na, 72,000 for mercury, 130,000 for Pb, and about 800,000 for Pt (see Table II.).

It must be emphasized that when a *neutral* atom (or molecule) escapes from the liquid, the energy lost in crossing the surface layer is equal to the work of cohesive forces only, that of the electric ones being obviously equal to zero. The electric double-layer does not, therefore, affect the vaporization heat, but permits us to calculate it, provided the above-mentioned connexion between the electric stress and the internal pressure is correct.

I hope to return to this question in a future paper.

Summary.

(1) Assuming the atoms to consist of positive nuclei with electrons rotating about them, it is shown that these electrons constitute over the surface of metals a layer of negative electrification with a corresponding layer of positive electri-

fication on the inner side of the surface, the electric double-layer of atomic thickness, thus formed, preventing the free electrons from escaping. The distribution of electric charge, intensity, and potential in the double-layer is calculated and the results generalized for all liquid and solid bodies.

(2) The *intrinsic potential* of the atomic double-layer is calculated for a few metals and shown to amount to a few volts and to increase with the valency, the valent electrons being the only ones effective in its production.

(3) The contact electromotive forces of metals and dielectrics are shown to be due to the difference of their intrinsic potentials.

(4) The surface-tension of liquids is accounted for by the *energy* of their atomic electric double-layers. The atomic radii and intrinsic potentials are calculated for a number of metals from their surface-tension.

(5) The intrinsic potentials thus calculated amount to a few volts and permit us to arrange the metals in Volta's series, while the atomic radii are very nearly equal to those corresponding, on Bohr's theory, to stationary orbits of second order.

(6) The small surface-tension of dielectrics, compared with metals, is explained and the surface-tension of liquid hydrogen is correctly calculated by means of Debye's model.

(7) The *normal stress* in the double-layer is calculated and its connexion with the internal pressure of liquids is pointed out.

In conclusion, I wish to express my thanks to Prof. A. Yoffé for his kind interest in this work.

Physical Institute of the Petrograd University,
December 6th, 1916.

XXXI. *The Secondary Potential of an Induction-Coil at "make."* By E. TAYLOR JONES, D.Sc., Professor of Physics in the University College of North Wales, Bangor*.

[Plate VII.]

THE chief interest attaching to a calculation of the potential at the secondary terminals of an induction-coil at "make" lies in the means which the result may suggest for the reduction of this quantity. In several of the processes in which induction-coil discharges are used, and

* Communicated by the Author.

especially in X-ray work, it is desirable to suppress the "inverse current" at make; and even if one of the usual rectifying devices is employed for the purpose—most of these are said to be but imperfect rectifiers—it is still important to reduce as far as possible the maximum potential to which the secondary terminals rise after contact is made at the interrupter. It need hardly be said, however, that in considering the various methods by which the make-potential may be reduced, the importance should be borne in mind of maintaining undiminished the potential at break. In the following calculation we shall regard the secondary circuit as open, and endeavour to find an expression for the make-potential in terms of the various coefficients of the two circuits.

Denoting the primary and secondary currents by i_1 , i_2 , the coefficient of induction of the primary coil on the secondary by L_{21} , that of the secondary on the primary by L_{12} , and with the usual notation for the other quantities, the equations are

$$L_1 \frac{di_1}{dt} + L_{12} \frac{di_2}{dt} + R_1 i_1 = E, \quad . \quad . \quad . \quad (1)$$

$$L_2 \frac{di_2}{dt} + L_{21} \frac{di_1}{dt} + R_2 i_2 + V_2 = 0, \quad . \quad . \quad . \quad (2)$$

$$i_2 = C_2 \frac{dV_2}{dt} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

It will be noticed that there is in these equations no term depending upon the capacity of the primary condenser. Although there is a very prevalent belief that the induced current in the secondary at make depends upon this capacity, which is said to "take up and store" the first rush of current, thus retarding the growth of current in the primary coil, it is difficult to understand how any such action can take place. At make, the condenser becomes short-circuited and, after losing its initial charge $C_1 E$ —none of which can pass through the coil—takes no further part in the proceedings. Experiment also shows that the primary condenser does not assist in reducing the secondary spark-length at make—at least this is certainly the case when the interval between break and make is not extremely short, so that the oscillations set up at break have time to die away before the following make. The condenser might indeed be expected to exert

* The secondary circuit being open and not connected with a condenser the current in it is not uniformly distributed along the wire. i_2 is the current in the central winding, and V_2 is the P.D. at the secondary terminals (see Phil. Mag. April 1914, p. 566).

some influence on the make-spark—increasing or diminishing its length—if the interruptions follow one another with very great rapidity, in which case there might be a considerable current flowing, one way or the other, in the primary coil at the moment of make. But in working conditions, chiefly owing to the fact that the secondary discharge at break usually causes rapid damping of the oscillations, this effect is not likely to be of importance, and in the present calculation we shall suppose that the initial value of the primary current at make is zero.

Denoting $i_1 = E/R_1$ by x , and making use of (3), equations (1) and (2) become

$$L_1 \frac{dx}{dt} + L_{12}C_2 \frac{d^2V_2}{dt^2} + R_1x = 0, \quad (4)$$

$$L_2C_2 \frac{d^2V_2}{dt^2} + L_{21} \frac{dx}{dt} + R_2C_2 \frac{dV_2}{dt} + V_2 = 0. \quad . . . (5)$$

The solution of equations (4), (5) is of the form $x = Ae^{zt}$, $V_2 = Be^{zt}$, where z is a root of the cubic equation

$$(L_1L_2 - L_{12}L_{21})z^3 + (L_1R_2 + L_2R_1)z^2 + \left(\frac{L_1}{C_2} + R_1R_2\right)z + \frac{R_1}{C_2} = 0. \quad . . . (6)$$

In all actual cases this equation will have two roots of the form

$$\left. \begin{aligned} z_1 &= -k_1 + 2\pi ni \dots \dots \dots \\ z_2 &= -k_1 - 2\pi ni \dots \dots \dots \end{aligned} \right\}, \quad (7)$$

where $i = \sqrt{-1}$, the third root being real, say

$$z_3 = -\delta, \quad (8)$$

The complete solution of (4), (5) is thus

$$\left. \begin{aligned} x &= A_1e^{z_1t} + A_2e^{z_2t} + A_3e^{z_3t} \dots \dots \dots \\ V_2 &= B_1e^{z_1t} + B_2e^{z_2t} + B_3e^{z_3t} \dots \dots \dots \end{aligned} \right\}, \quad . . . (9)$$

where the A 's and B 's are to be determined from the initial conditions. These are $i_1 = 0$, $V_2 = 0$, $i_2 = 0$, that is

$$x = -E/R_1, \quad V_2 = 0, \quad \frac{dV_2}{dt} = 0, \quad \text{when } t = 0. \quad . . . (10)$$

Thus, by (9)

$$\left. \begin{aligned} \Sigma A &= -E/R_1 \dots \dots \dots \\ \Sigma B &= 0 \dots \dots \dots \\ \Sigma Bz &= 0 \dots \dots \dots \end{aligned} \right\} \quad (11)$$

Since each particular solution satisfies equations (4) and (5) we have, on substituting and adding,

$$\begin{aligned} L_1 \Sigma A z + L_{12} C_2 \Sigma B z^2 + R_1 \Sigma A &= 0, \\ L_2 C_2 \Sigma B z^2 + L_{21} \Sigma A z + R_2 C_2 \Sigma B z + \Sigma B &= 0, \end{aligned}$$

which by (11) give

$$\Sigma A z = - \frac{L_2 C_2}{L_{21}} \Sigma B z^2,$$

and

$$\begin{aligned} \Sigma B z^2 &= - \frac{E L_{21}}{C_2 (L_1 L_2 - L_{12} L_{21})} \\ &= - \frac{E L_{21}}{C_2 L_1 L_2 (1 - k^2)} \\ &= G, \text{ say.} \end{aligned}$$

Here k is the coefficient of coupling of the primary and secondary circuits, that is, $k = \sqrt{L_{12} L_{21} / L_1 L_2}$. Thus the equations for the B's are

$$\left. \begin{aligned} B_1 + B_2 + B_3 &= 0 \dots \\ B_1 z_1 + B_2 z_2 + B_3 z_3 &= 0 \dots \\ B_1 z_1^2 + B_2 z_2^2 + B_3 z_3^2 &= G \dots \end{aligned} \right\} \dots \dots \dots (12)$$

Similarly, for the A's the equations are

$$\left. \begin{aligned} \frac{A_1}{z_1} + \frac{A_2}{z_2} + \frac{A_3}{z_3} &= \frac{E L_1}{R_1^2} \dots \dots \dots \\ A_1 + A_2 + A_3 &= - \frac{E}{R_1} \dots \dots \dots \\ A_1 z_1 + A_2 z_2 + A_3 z_3 &= \frac{E}{L_1 (1 - k^2)} \dots \end{aligned} \right\} \dots \dots (13)$$

Along with (6) equations (13) enable us to find the primary current and equations (12) the secondary potential at any time after make; it is the latter quantity that we are concerned with here.

Solving (12) for B_1 , we find, after reduction,

$$B_1 = - \frac{G}{(z_1 - z_2)(z_3 - z_1)},$$

which by (7) and (8) becomes

$$\begin{aligned} B_1 &= - \frac{G}{4\pi n} \cdot \frac{1}{2\pi n + (k_1 - \delta)i} \\ &= - \frac{G}{4\pi n} \cdot \frac{2\pi n - (k_1 - \delta)i}{4\pi^2 n^2 + (k_1 - \delta)^2}. \end{aligned}$$

We may neglect $(k_1 - \delta)^2$ in comparison with $4\pi^2 n^2$ so that

$$B_1 e^{z_1 t} = - \frac{G e^{-k_1 t}}{4\pi n} \cdot \frac{2\pi n - (k_1 - \delta)i}{4\pi^2 n^2} (\cos 2\pi n t + i \sin 2\pi n t).$$

The real part of this is

$$\begin{aligned} & - \frac{G e^{-k_1 t}}{4\pi n \cdot 4\pi^2 n^2} \{2\pi n \cos 2\pi n t + (k_1 - \delta) \sin 2\pi n t\} \\ & = - \frac{1}{2} \cdot \frac{G e^{-k_1 t}}{4\pi^2 n^2} \cos (2\pi n t - \theta), \quad . \quad . \quad . \quad . \quad (14) \end{aligned}$$

where $\tan \theta = \frac{k_1 - \delta}{2\pi n}.$

Similarly we find that the real part of $B_2 e^{z_2 t}$ is also equal to the expression (14), while B_3 is real and equal to $G/4\pi^2 n^2$. Thus the complete solution for V_2 is

$$V_2 = - \frac{G}{4\pi^2 n^2} \{e^{-k_1 t} \cos (2\pi n t - \theta) - e^{-\delta t}\}.$$

Now the approximate value of $4\pi^2 n^2$, obtained by neglecting the effect of the resistances on the frequency, is $\frac{1}{L_2 C_2 (1 - k^2)}$; that is, the frequency is that of the secondary circuit with the primary closed. Thus $G/4\pi^2 n^2 = -EL_{21}/L_1$, and finally

$$V_2 = \frac{EL_{21}}{L_1} \{e^{-k_1 t} \cos (2\pi n t - \theta) - e^{-\delta t}\} \quad . \quad . \quad (15)$$

The wave of potential in the secondary circuit at make thus consists of a damped oscillation superposed upon an exponentially decaying part, the initial values of the two parts being $\pm EL_{21}/L_1$. The greatest numerical value of the expression (15) for V_2 occurs at a time t_1 somewhat less than $1/2n$, and will in all cases be less than $2EL_{21}/L_1$, the value of the maximum when k_1 and δ are zero. The expression $2EL_{21}/L_1$ may be regarded as giving the limiting value of the maximum potential at make, to which the actual value would approximate if k_1 and δ were indefinitely reduced. In actual cases, however, k_1 and δ are probably never so small as to allow the above limit to be very closely approached.

According to (15) the secondary potential at make is proportional to the battery E.M.F. in the primary circuit, but it depends to a much smaller extent (only through k_1 and δ) on the resistance in this circuit. These results agree with the indications of the secondary spark at make. For example, a certain 18-inch coil, excited by a slow interrupter worked by hand, gave at $E = 20$ volts, $R_1 = 10$ ohms, a make-spark about 0.7 mm.

long. With a battery of 98 volts and the same resistance in the primary circuit the spark-length at make was 4.5 mm. These sparks passed between two ball electrodes each 2 cm. in diameter, and therefore represent potentials of about 3500 and 16000 volts respectively. When the primary resistance was increased to 50 ohms the spark-length at make ($E=98$ volts) only fell to 3.7 mm.

Thus the potential at make increases rapidly with the battery E.M.F., but only varies slightly with the primary current. On the other hand, the potential at break depends greatly upon the primary current, being proportional to the value of this current at the moment of interruption. Consequently it is desirable in working an induction-coil, with a view to reducing the secondary potential and the inverse current at make, to employ the smallest battery that is sufficient to produce the required potential at break. Frequently, however, an induction-coil is for reasons of convenience worked from a source at constant potential, such as the 100-volt or 200-volt supply-mains, through a series regulating resistance, in which case there is no possibility of adjusting E . In any case, whatever be the source of supply, it is desirable to consider what other means there may be for reducing the potential at make.

The expression (15) for the potential at make contains the factor L_{21} , and the potential may accordingly be reduced by diminishing the mutual inductance of the primary and secondary coils. This may be effected without causing any alteration in L_1 by withdrawing the primary and the core axially from their symmetrical position in the secondary. In addition to reducing L_{21} such a displacement has the effect of diminishing L_2C_2 , and consequently also the period of the oscillation. Thus the time t_1 during which the damping forces act before the maximum make-potential is attained is diminished, and this tends to increase the maximum. On the whole, however, the withdrawal of the primary is found to have the effect of reducing the spark-length at make. On one occasion, for example, the 18-inch coil with the primary in the position of maximum mutual inductance gave a make-spark 4.4 mm. long ($E=98$ volts, $R_1=12$ ohms). When the primary was drawn out 30 cm. from this position the spark-length at make was only 1.5 mm.

It might be thought that the displacement of the primary coil would, owing to the decrease of mutual inductance which it entails, cause a diminution of the secondary spark-length at break, but this is not necessarily the case. By drawing out the primary the system may be brought into one of the

adjustments which are most favourable to the conversion of magnetic energy of the primary current into electrostatic energy in the secondary circuit*. In one of these adjustments the coefficient of coupling is determined by $k^2=0.57$, the primary capacity by $L_1C_1=0.43 L_2C_2$. If the primary is drawn out to this position, and the capacity of the primary condenser adjusted to its optimum value, the electrostatic energy generated in the secondary circuit (for a given value of the primary current) will be at its maximum. The position of the primary which gives maximum secondary potential will probably be influenced to some extent by the reduction of capacity of the secondary coil due to the displacement of the primary†.

In the case of the 18-inch coil above referred to, whether worked by the slow break or by a motor interrupter, the spark-length at break is distinctly increased by drawing out the primary to a distance of 30 cm. from its symmetrical position. It is worthy of note that if an X-ray tube is connected to the secondary terminals the mean current through the tube, as indicated by a moving-coil milliampere meter, is less, but a fluorescent screen on which the rays fall glows more brightly, in the displaced than in the symmetrical position.

Thus the process of reducing the mutual inductance by drawing out the primary coil to a suitable distance along the axis of the secondary not only materially reduces the negative secondary potential at make, but also increases the positive potential at break.

According to (15) the secondary potential at make is, other things being the same, inversely proportional to L_1 , the self-inductance of the primary circuit, and may be reduced by connecting an inductance-coil in series with the primary and the battery. Thus the addition of an air-core coil of about 0.07 henry to the primary circuit of the 18-inch coil, the total resistance of the primary circuit (10 ohms) being kept constant, reduced the make-spark from 4.5 mm. to 2.7 mm. The effect is even more marked when the four layers of the primary coil are connected in parallel, L_1 being now much smaller to begin with. The insertion of the air-core coil now reduces the spark-length at make from 13.1 to 1.0 mm.

* Phil. Mag. Jan. 1915, pp. 1-4.

† The same effect—a maximum of secondary potential at break in a certain displaced position of the primary coil—is also observed when the secondary terminals are connected to a condenser, in which case the change of C_2 due to the displacement of the primary is insignificant.

The addition of series inductance to the primary circuit exerts a minor influence on the secondary potential at make in two other ways, viz.:—(1) Since k^2 is diminished the period $2\pi\sqrt{L_2C_2(1-k^2)}$, and with it the effective time of action t_1 of the damping forces, is increased; this tends to reduce the maximum potential V_{2m} : (2) the ratio R_1/L_1 , and therefore also k_1 and δ , may be altered; e.g., if R_1 is kept constant k_1 and δ are reduced; this tends to increase V_{2m} . In all ordinary circumstances these two effects are probably much smaller than the first.

The series inductance also increases the secondary potential at the *interruption* of a given primary current, and increases the spark-length of the coil for a given mean primary current. These effects arise not only from the fact that the magnetic energy at break is increased by increasing L_1 , but also because the coupling may be thus reduced to a certain point without loss—and generally with gain—of efficiency of conversion of primary magnetic into secondary electrostatic energy*. Thus the process serves the double purpose of increasing the potential at break and diminishing the potential at make.

It is a well-known fact, first observed by Duddell †, that inverse current through an X-ray tube also sometimes appears at *break*. In this case it appears to be due to a kind of delayed discharge, the discharge failing to pass in the first half-oscillation after break, but passing in the second, or negative, half-oscillation. As far as the writer has observed, this effect can be prevented by sufficiently increasing the positive potential at break: the higher this is the less likely is the discharge to be delayed beyond it. Thus the use of series inductance in the primary circuit tends to prevent the occurrence of inverse current at both make and break.

In some coils there is another way in which the primary self-inductance can be changed, viz.: by connecting the layers of the primary coil in series or in parallel or in other ways. If the layers be regarded as all having the same magnetic effect (for the same current), these changes of connexion do not affect the coefficient of coupling, though the mutual inductance and the primary self-inductance themselves are greatly altered. For example, if there are four layers and the connexion is changed from series to parallel, L_{21} and L_{12} are reduced to one quarter, L_1 to one sixteenth, of their original values. Thus k^2 is unaltered while L_{21}/L_1 is increased to four times its original value. If acting alone this would, by (15), increase the secondary potential at make

* Phil. Mag. Aug. 1915, pp. 233–235.

† Journ. Rönt. Soc. vol. iv. 17, p. 7 (1908).

in the ratio 4/1. But if the total primary resistance R_1 is maintained at its original value, the ratio R_1/L_1 is increased in the ratio 16/1, and consequently the damping factors k_1 and δ are greatly increased, and this tends to reduce V_{2m} . On the whole, however, there is usually a very marked increase in the spark-length at make when the primary connexion is changed from series to parallel. Thus, with the four primary layers of the 18-inch coil in series ($E=98$ volts, $R_1=10$ ohms) the spark-length at make between the ball electrodes was 4.5 mm.; with the layers in parallel and the same values of E and R_1 the spark-length was 13.1 mm. If, instead of keeping R_1 constant, the resistance were reduced in the same ratio as L_1 , the difference between the series and parallel connexions would be still greater, owing to the fact that k_1 and δ are then unaltered by the change of connexion.

The nature and to some extent the magnitude of the above effects may be illustrated by the following numerical results, in which the values of n , k_1 , and δ are calculated from the cubic equation (6). It should be borne in mind that the coefficients of equations (4) and (5), *i. e.* the inductances and resistances, are not strictly constant, but are mean values for the time-interval t_1 immediately after "make," and that during this short time the primary current does not rise to more than a small fraction of its maximum value, so that the core is not strongly magnetized and its permeability is small. The values here assumed are typical of a fairly large (18- or 20-inch) coil.

The expression in the brackets of (15), with sign changed, that is, $-e^{-k_1 t} \cos(2\pi n t - \theta) + e^{-\delta t}$, is denoted by ϕ , its maximum value by ϕ_m .

The following values are common to all the cases :—

$$L_{21}/L_1=100, \quad k^2=0.75, \quad L_2 C_2=7.66 \cdot 10^{-8} \text{ c.g.s.},$$

$$C_2=0.000053 \text{ mfd.}, \quad R_2=40000 \text{ ohms},$$

$$E=100 \text{ volts.}$$

$$(I.) \quad R_1=13 \text{ ohms}, \quad L_1=0.145 \text{ henry}, \quad R_1/L_1=89.6.$$

$$\text{By (6)} \quad 2\pi n=7220, \quad k_1=191.5, \quad \delta=88.5,$$

$$\phi_m=1.883, \quad V_{2m}=18830 \text{ volts.}$$

$$(II.) \quad R_1=8 \text{ ohms}, \quad L_1=0.145 \text{ henry}, \quad R_1/L_1=55.2,$$

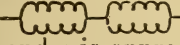
$$2\pi n=7223, \quad k_1=139.5, \quad \delta=52.5,$$

$$\phi_m=1.918, \quad V_{2m}=19180 \text{ volts.}$$

These two examples illustrate the effect of reducing the primary resistance. The difference of 5 ohms causes a considerable reduction in k_1 and δ ; but since these quantities are already rather small, the effect on ϕ_m , and therefore on

the maximum secondary potential at make, is not great. Measurements of the spark-length at make show that if R_1 is reduced from a large value the potential at first increases, but it reaches a limiting value after which further reduction of R_1 causes no change.

$$\begin{aligned} \text{(III.) } R_1 &= 13 \text{ ohms, } L_1 = 0.03625 \text{ henry, } R_1/L_1 = 358.4, \\ 2\pi n &= 7174, \quad k_1 = 591.1, \quad \delta = 363, \\ \phi_m &= 1.629, \quad V_{2m} = 32580 \text{ volts.} \end{aligned}$$

This case and the first illustrate the effect of reducing L_1 to one quarter, as by connecting the primary layers in series-parallel . The effect is to increase greatly k_1 and δ , and n is appreciably reduced. ϕ_m is reduced, but L_{21}/L_1 is doubled, so that there is a considerable increase of spark-length.

$$\begin{aligned} \text{(IV.) } R_1 &= 13 \text{ ohms, } L_1 = 0.00906 \text{ henry, } R_1/L_1 = 1437, \\ 2\pi n &= 6404, \quad k_1 = 2101, \quad \delta = 1646, \\ \phi_m &= 0.861, \quad V_{2m} = 34440 \text{ volts.} \end{aligned}$$

This case, when compared with the first, shows the effect of changing from the series to the parallel connexion, L_1 being thus reduced to one sixteenth. k_1 and δ become very great, and the effect on n is considerable. ϕ_m is reduced to less than one-half, but since L_{21}/L_1 is quadrupled, V_{2m} is nearly doubled as compared with case I.

The maximum potentials in cases (III.) and (IV.) are not very different in value, the increase of the factor L_{21}/L_1 being nearly compensated by the increase of k_1 and δ . This relation depends upon the value of R_1 , as is shown by the following measurements of spark-length (Table I.). In each case the battery E.M.F. was 98 volts, the numbers giving the spark-length at make, in millimetres, between the ball electrodes.

TABLE I.

| R_1 ohms. | Spark-length in millimetres. | |
|----------------|------------------------------|-----------|
| | Series-parallel. | Parallel. |
| 10 | 8.8 | 14.3 |
| 16 | 7.8 | 9.5 |
| 25 | 6.6 | 6.6 |
| 35 | 6.0 | 4.9 |

Thus when R_1 is small the parallel connexion gives a longer make-spark than the series-parallel. The reverse is the case when R_1 is large. With the coil used in these experiments the effects are equal at the value $R_1 = 25$ ohms.

It may be remarked here that *for a given P.D. at the primary terminals* the spark-length at *break* is also greatest when the primary layers are in parallel. This results, of course, from the large value of the primary current. Considering, for example, the change from series to parallel, L_1 and R_1 are both reduced to one sixteenth, L_{21} to one-quarter, of their "series" values. Thus the primary current at break

—given approximately by $\frac{E}{R_1}(1 - e^{-\delta T})$, where T = time of

contact—is increased to sixteen times, and $L_{21}i_0$ to four times, its original value. The coefficient of coupling being unchanged, the primary capacity being supposed in each case to be the optimum, and the effect of damping being regarded as unaltered, the secondary potential is proportional to $L_{21}i_0$, and is therefore quadrupled. On the other hand, if the coil is driven through a considerable series regulating resistance, the spark-length at break is greatest when the layers are in series. In this case the lowering of resistance due to the change from series to parallel is of little consequence, and the diminution of L_{21} reduces the secondary potential.

The effect on the potential at make of varying the primary self-inductance is further illustrated by the three oscillograph photographs shown in figs. 1, 2, and 3 (Plate VII.). In obtaining these the coil was worked by a motor interrupter, the oscillograph being connected directly to the secondary terminals. Each photograph shows a "make" followed by a "break," the movement being from right to left. In each case the 98-volt battery was used, the total primary resistance R_1 being 46.7 ohms. This rather large value of R_1 was employed in order to reduce the secondary potential at *break*. If R_1 is increased the break-potential, being proportional to the primary current immediately before interruption, falls off more rapidly than does the make-potential. The break-potential was further reduced by employing a large primary capacity—10 microfarads, a value far greater than the optimum. The interval between make and break is in each photograph 0.00936 sec. The deflexion from the zero line is proportional to the square of the secondary potential.

Fig. 1 shows the curve obtained when the primary coil was connected in the series-parallel arrangement (*cf.* case III. above). The potential at make is greater than that at

break, the maximum value indicated being approximately 17500 volts.

In fig. 2 the four layers of the primary coil were all in series, and the maximum potential at make is reduced to 14000 volts.

In the case of fig. 3 the air-core coil (0.07 henry) was connected in series with the primary, the layers of which were still in series. The maximum potential at make is now reduced to only 9600 volts. In this case the coefficient of coupling has approximately the value which, when the primary capacity is adjusted to its optimum value, allows the maximum ratio of conversion of magnetic into electrostatic energy at break. The make-potential of 9600 volts would scarcely suffice to generate any inverse current through an X-ray tube, and it may be remarked that in the case of fig. 3 the make-potential would not be appreciably increased if the primary resistance were much reduced for the purpose of increasing the potential at break.

As to the absolute value of the make-potential given by the expression (15), if the resistances of the circuits are taken at their steady-current values, the calculated value of V_{2m} is rather greater—about 15 per cent. in the present experiments—than the value found experimentally. The principal reason for this is undoubtedly that the value of k_1 , the damping factor of the oscillation, is greater than that calculated from the steady-current resistances. The oscillation also undergoes decay in consequence of core losses.

The effect of one other variation of the system may be briefly referred to. According to (15) the secondary capacity has only an indirect influence on the spark-length at make. If this capacity is increased—*e. g.* by connecting a leyden-jar to the secondary terminals—the period of the oscillation, and with it the time t_1 of rise to maximum potential, is lengthened. The damping forces have therefore a longer time in which to act, and a reduction of V_{2m} is to be expected. This reduction will be but slight if k_1 and δ are small, that is, if R_1/L_1 is small. The effect might be expected to be greater if R_1/L_1 is large. These conclusions are borne out by measurements of the spark-length at make with and without a secondary condenser. Thus, with the primary layers in series ($E=82$ volts, $R_1=16$ ohms, $R_1/L_1=110$), connecting a 0.001 mfd. jar to the secondary terminals (which causes a twenty-fold increase of C_2) only reduced the make-spark from 3.8 to 3.4 mm. When R_1 was increased to 41 ohms the addition of the jar reduced the spark from 3.5 to 2.3 mm.; when R_1 was 82 ohms the reduction was from 3.0 to 1.5 mm.

Again, with the four primary layers all in parallel and $R_1 = 13.7$ ohms ($R_1/L_1 = 1500$) the jar reduced the make-spark from 9.0 to 3.9 mm. With $R_1 = 6.85$ ohms ($R_1/L_1 = 750$) the jar diminished the spark from 13.2 to 6.6 mm.

The secondary condenser doubtless acts also in another way in modifying the secondary potential at make; it alters the effective resistance of the secondary circuit, which depends to some extent on the frequency of the oscillation. In all cases, however, it would appear that the condenser only affects the make-potential by altering the effect of the damping forces. The action of a secondary condenser in varying the secondary potential at *break* is of an entirely different nature, and arises from a different cause. This question will be considered on a future occasion.

Bangor, February 1917.

XXXII. *Magnetic Hysteresis treated according to Van der Waals's Equation and the Kinetic Theory.* By J. R. ASHWORTH, D.Sc.*

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* Communicated by the Author.

I.

1. **I**N a paper, published in this Magazine in November 1915, on "The Application of Van der Waals's Equation to Magnetism" *, Curie's views † on the analogy between the intensity of a paramagnetic material as a function of field-strength and temperature and the density of a gas as a function of the pressure and temperature were discussed and extended, and it was shown that the relation of ferromagnetism to paramagnetism may be regarded as analogous to that of a liquid to its vapour. In short, just as we consider the gas law

$$\frac{P}{\rho} = RT$$

as a special case of the more general equation

$$(P + a\rho^2) \left(\frac{1}{\rho} - \frac{1}{\rho_0} \right) = RT,$$

where P , ρ , and T are the pressure, density, and absolute temperature of the gas, and a , ρ_0 , and R are constants, so we may treat the paramagnetic law

$$\frac{H}{I} = R'T$$

as a special case of a more general equation,

$$(H + a'I^2) \left(\frac{1}{I} - \frac{1}{I_0} \right) = R'T, \quad . \quad . \quad . \quad (1)$$

where H , I , and T are field-strength, intensity of magnetization, and absolute temperature respectively, and a' , I_0 , and R' are constants corresponding to the constants a , ρ_0 , and R in the fluid equation. The general equation to fluids applies to liquids when the density is large, and to gases or vapours when the density is small; and in the same way the general equation to magnetism applies to ferromagnetism when the intensity of magnetization is large, and to paramagnetism when it is very small.

In the paper to which reference has been made, the application of these views of the ferromagnetic and paramagnetic states was considered in so far as intensity of magnetization is dependent on temperature, and values for the constants a' , I_0 , and R' were obtained for each of the

* Ashworth, Phil. Mag. vol. xxx. p. 711 (1915).

† Curie, '*Œuvres*,' p. 330.

ferromagnetic elements—iron, nickel, and cobalt, but consideration of the relation of intensity of magnetization to field-strength was deferred. It is the object of the present paper to trace the results of applying the magnetic equation to the intensity (I) as a function of the field (H).

2 In the passage of a vapour to the liquid state along an isothermal, below the critical temperature and critical pressure, there are three well-marked stages. In the first the vapour is of small density, and, until it approaches saturation, it deviates but little from the gas law; in the second there is an abrupt and very large increase of density in the passage to the liquid state; and in the third stage the density of the liquid increases slowly with pressure, and finally approaches a constant value at high pressures.

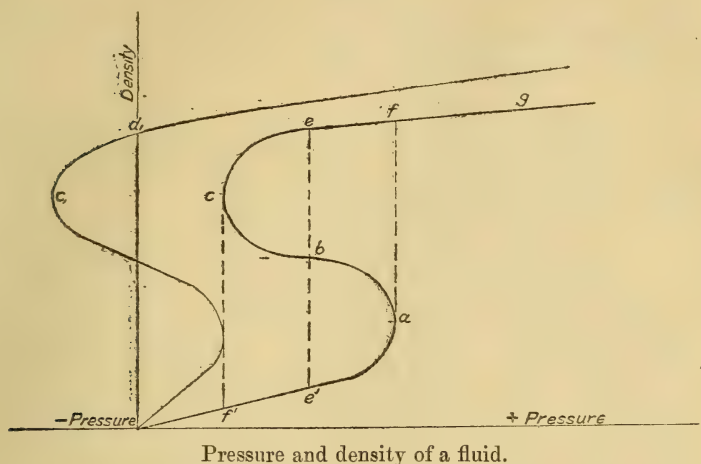
Ewing has remarked that the curve of magnetization is characterized by three stages. In the first there is a growth of magnetism as the field increases which is small and nearly proportional to the field; in the second there is a rapid and large increase of magnetic intensity for a very small change of field-strength; and in the third stage the magnetism augments very slowly and at a diminishing rate, so that in strong fields the intensity becomes nearly constant.

In fluids, as the temperature rises, the second stage becomes shorter and shorter and disappears at the critical temperature; and, similarly, in magnetism, as the temperature increases, the second stage grows less and less and vanishes at the critical temperature. Thus there is a general agreement in the manner in which fluid-density increases with pressure both below and above the fluid critical temperature and the manner in which magnetic intensity increases with field-strength both below and above the magnetic critical temperature.

3. The sudden change of density which takes place when a saturated vapour abruptly condenses to a liquid is not now regarded as a discontinuity, but is treated as the passage from one state to the other by a continuous path having a double inflexion in it as in the figure (fig. 1, $e' a b c e$). Tracing this isothermal, we have the fluid in the first stage from 0 to e' as vapour; at e' the vapour is saturated, and the second stage begins with abrupt transition to e , and from e to f and onwards we have the third stage. Under certain conditions, particularly freedom from disturbance, the fluid may follow the path from e' towards a , and also, on returning from liquid to vapour, the fluid may continue along the path

from e towards c , but the part $a b c$ cannot be experimentally realized, as the fluid in that region is in an unstable state.

Fig. 1.



For isothermals corresponding to higher temperatures than the one traced, the part between e and e' diminishes, and finally disappears at the critical temperature, at which point there is a critical density and a critical pressure. For lower isothermals than the one drawn, it is possible for the point c to touch the axis of no pressure and even to pass to the other side as at c_1 , and the liquid then exists under a negative pressure.

If the fluid were to follow the path $e' a$, it would reach the limit of stability at a , and would then pass suddenly to f ; and in the same way, if it were made to traverse the path $f e c$, it would reach another limit of stability at c and would suddenly change to f' . In such a cyclic change the loop $f' a f c f'$ would be traced out, and there would be a loss of energy as the fluid was made to pass from vapour to liquid and back to vapour, giving rise to what may be called fluid hysteresis loss; and, on the other hand, when no precautions are taken to preserve the fluid from disturbance, the path $f' e' e f$ is followed to and fro, and there is no dissipation of energy. The path is then anhysteretic. Van der Waals's equation, which is a cubic in ρ (the density), represents with considerable success the shape of the fluid isothermals, and gives a satisfactory account of the critical constants.

Now the ferromagnetic equation is a repetition of Van der Waals's equation, and it must give to the magnetic isothermals similar forms to those which have been discussed.

The equation is a cubic in I , the intensity, and, therefore, the rapid augmentation of intensity in the second stage may be regarded as continuous along a curved path with a double inflexion in it. It is this double inflexion of the isothermal, having two stable parts joined by an unstable portion, which gives rise to magnetic hysteresis.

4. According to these views, we should expect to find not only a critical temperature (T_c) but also a critical intensity (I_c) and a critical field (H_c), expressions for which are easily obtained from the ferromagnetic equation.

There is ample evidence that a critical temperature (or temperature-interval) exists for magnetism, and the evidence for a critical intensity is clear if we regard this intensity as the point where ferromagnetic qualities change to paramagnetic qualities at the critical temperature—in other words, where the critical isodynamic changes its curvature. The evidence for a critical field is, however, not quite so obvious; but, as Curie pointed out*, there is at low fields an abrupt change of direction of the isothermal just below the critical temperature from being nearly vertical to being nearly horizontal, whilst just above the critical temperature the isothermals are straight lines inclined at a small angle to the axis of H . In the angular space, included between the horizontal and inclined isothermals, there must be some field for which the abruptly changing isothermal passes to the smooth linear isothermal, and this may be treated as the critical field.

5. The specific properties of any ferromagnetic body depend on the values assigned to the constants α' , I_0 , and R' ; but, by eliminating these quantities, a reduced equation can be obtained which gives the relations of I , H , and T in their most general form. Such an equation can be written by treating I , H , and T as functions of the critical constants or of some other well-defined values. Thus let

$$l = \frac{H}{H_c}, \quad m = \frac{I}{I_0}, \quad \text{and} \quad n = \frac{T}{T_c},$$

where I_0 is the maximum value of the intensity and is equal to $3I_c$; then the reduced equation is

$$(l + 27m^2) \left(\frac{1}{m} - 1 \right) = 8n. \quad . \quad . \quad . \quad (2)$$

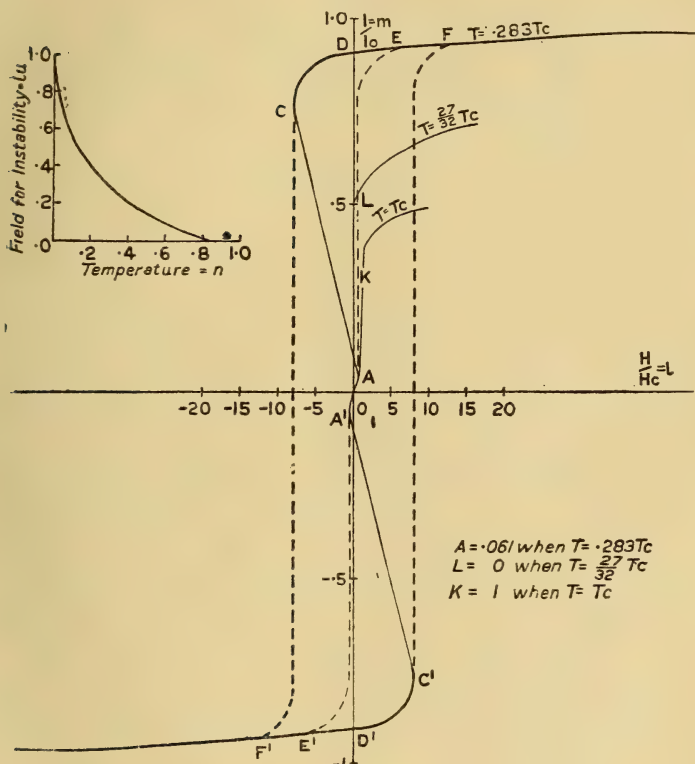
We can trace the reduced curve of $I = \phi(H)$ from this

* Curie, *Œuvres*, p. 309.

equation (see fig. 2). For example, when $n=0$ then $m=1$, and the intensity has its maximum value; when $l=0$ the equation is a quadratic in m , and

$$m = \frac{1 \pm \sqrt{1 - \frac{32}{27}n}}{2} \dots \dots \dots (3)$$

Fig. 2.



Reduced hysteretic and anhysteretic magnetic isothermals.

The upper of the two values for m is a stable one, and is that of the reduced residual magnetic intensity (m_r); the lower value is on the unstable part of the curve.

The point where the curve changes from a stable to an unstable stage is where $\frac{dm}{dl}$ is equal to infinity.

Now
$$\frac{dm}{dl} = \frac{1-m}{\frac{l}{m} - 27m(1-2m)}; \quad . \quad . \quad . \quad (4)$$

and this is infinity when the denominator is zero. Hence

$$l_u = 27m_u^2(1-2m_u), \quad . \quad . \quad . \quad (5)$$

l_u and m_u being values where instability begins. This value of l_u is negative when m_u is greater than 0.5 or n less than 27/32.

From this equation l_u can be determined when m_u is known. Now m_u is known when the temperature is chosen, for, by substituting $27m_u^2(1-2m_u)$ for l in the reduced equation (2), we get

$$m_u(1-m_u)^2 = \frac{4}{27}n, \quad . \quad . \quad . \quad (6)$$

a relation which allows m_u to be calculated for any assigned reduced temperature n .

6. The curve is traced in fig. 2 for $n=0.283$, which is equivalent to 300°A. or 27°C. when the critical temperature is that for iron, namely 785°C. The residual magnetic intensity (m_r) is then 0.905 of the maximum intensity (I_0), and instability begins when $m=0.76$.

The maximum reduced field for instability (l_u) is -8.1 . Below $m_u=0.76$ the intensity is in an unstable state as far as $m=0.05$ (l being then $+0.061$), when instability again passes to stability and the curve finally descends to the origin. The unstable part of the curve crosses the axis at $m=0.092$.

The curve is traced in the figure in a similar manner for negative values of the intensity.

Suppose we follow the path of stable values of the reduced magnetic intensity (m), and begin by applying a strong positive magnetic field so that m is very large; then, as the field diminishes to zero, m falls slowly to the point D, where it has the residual value; and after that, when the field becomes negative, the curve droops more and more rapidly to the initial point of instability C. The magnetic intensity must then very rapidly pass to the next stable position, if it has not done so before, consistent with the existing negative field, and this is the point F' on the negative side of the axis of intensity.

As the negative field is brought back through zero to its

former positive value, the negative magnetic intensity passes its residual value at D' , reaches a point of instability at C' , and again rapidly changes to a high positive value at F , thus completing a *hysteresis loop*.

The reduced field l_u corresponding to the point C is the same as the maximum reduced coercive force if the magnetic intensity falls abruptly at this point through zero to its stable negative value.

7. By means of equations (5) and (6) the variation with temperature of l_u , the reduced field for instability corresponding to the point C , can be determined. This has been done, and is shown in the inset to fig. 2, from which it is seen that the reduced field falls rapidly at first, but at a diminishing rate, as the temperature progresses until it reaches zero, when the temperature is $27/32T_c$, and the residual intensity is equal to $\frac{1}{2}I_0$.

The hysteresis loop thus shrinks in area with rise of temperature.

If we put $l_u = H_u/H_c$ in equation (5), and write

$$H_c = \frac{1}{27} a' I_0^2, \quad . \quad . \quad . \quad . \quad . \quad (7)$$

then

$$H_u = a' I_0^2 m_u^2 (1 - 2m_u), \quad . \quad . \quad . \quad . \quad (8)$$

which shows that the field for instability depends on the maximum intrinsic field ($a' I_0^2$), and on m_u which is a function of the temperature.

8. If the analogy between fluid and magnetic hysteresis is once more recalled, we see that in fluids hysteresis is not usually in evidence, and it can only be observed under special conditions; on the contrary, in magnetism it is always prominent, and it is only under special conditions that it can be suppressed. In both fluids and magnetism freedom from disturbance is favourable to the exhibition of hysteresis, and agitation of any kind reduces it and may even annul it. For example, when a ferromagnetic body is subjected to mechanical agitation or to an alternating current, hysteresis is suppressed partly or completely. Under these circumstances magnetism is acquired with very great facility on the application of a very small field, and the susceptibility is then enormously great. In fig. 2 the broken line drawn nearly parallel and close to the vertical axis represents theoretically an anhysteretic curve of magnetization, and

this is the analogue of the straight line in the density-pressure diagram of a fluid which represents the sudden condensation from saturated vapour to liquid. Thus the anhysteretic isothermal finds its place, according to theory, side by side with the two branches of the hysteretic loop.

This view naturally leads to the inquiry whether a latent heat exists for magnetism as for fluids. If there is a latent heat it is probably very small, for a reason which will be given later in discussing the character of the intrinsic field.

9. For the stable parts of the isothermals there will be a reduced field-coefficient of magnetic intensity (a_l), which may be written

$$a_l = \frac{1}{m} \frac{dm}{dl},$$

$$= \frac{1-m}{l-27m^2(1-2m)} \cdot \cdot \cdot \cdot \cdot \quad (9)$$

This is applicable to any ferromagnetic substance, and it follows that equal reduced intensities ought to be found for the same reduced fields at corresponding temperatures.

Experiments on this subject are in progress.

A corresponding proposition in the relations of magnetic intensity to temperature has been shown to be true at least for residual magnetism.

10. We may add here that the ferromagnetic equation, being a cubic in I , shows that there should be hysteresis in the relation of intensity of magnetization to temperature as there is hysteresis in the relation of intensity of magnetization to field-strength. It is easy to demonstrate from the reduced equation that when $l=1$ and the temperature is the critical temperature, then $m = \frac{1}{3}$, and that for values of n

and of l less than unity there are on any isodynamic two stable values of m , at two respective temperatures, between which there is an unstable region where hysteresis effects are possible. Experiments show that there is hysteresis with temperature in general*, and it is usually prominent when hysteresis in relation to field-strength is pronounced.

* Honda & Takagi, Sci. Reports Tohoku Univ., Sendai, Japan, vol. i. no. 4, p. 213 (1912).

II.

In this part the relation $I = \phi(H)$ will be treated from the standpoint of the kinetic theory.

Langevin's equation for a paramagnetic substance* is

$$I/I_0 = \coth x - \frac{1}{x}, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where
$$x = \frac{\mu \cdot H}{RT},$$

μ being the magnetic moment of the molecule, H the field, T the absolute temperature, and R the gas constant.

Weiss supposes the mutual action of the magnetic molecules in a ferromagnetic body to be equivalent to that of a uniform field proportional to the intensity of magnetization†. Thus the intrinsic or molecular field H_i may be written $H_i = NI$, where N is a constant, and if this field be added to H the expression for x becomes

$$x = \frac{\mu(H + NI)}{RT}, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

which gives
$$I = \frac{RT}{\mu N} x - \frac{H}{N}, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

a linear equation in I and x for any given temperature.

2. In fig. 3 the curve OCDJR is the graph of equation (1), and the straight lines represent equation (3) for given temperatures and fields, the tangent of the inclination of the line to the x -axis being given by $\frac{R}{\mu N} T$, and the intercept which the line makes with the vertical axis being $\frac{H}{N}$. The intensity of magnetization for any given temperature and field is determined by the intersection of the curve with the straight line since the intensity must satisfy simultaneously both equations.

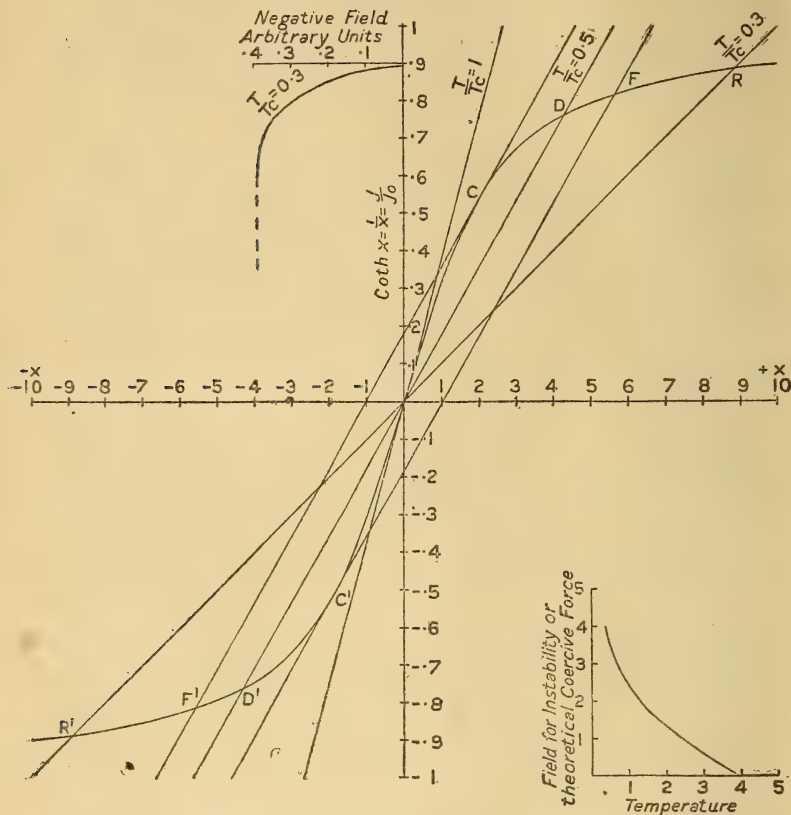
Weiss treats H as negligible in comparison with NI (for all but very low values of I), and the straight line therefore passes through the origin. By varying the slope of the line he traces the relation of intensity to temperature, but he leaves the relation of intensity to field-strength out of consideration.

* Langevin, *Ann. Chim. Phys.* ser. 8, t. v. p. 70 (1905).

† Weiss, *C. R.* t. cxliii. no. 26, p. 1136, Dec. 1906.

3. Suppose, however, that H is not ignored in equation (3), then the straight line representing this equation will not in general pass through the origin.

Fig. 3.



Thus, at a given temperature the isothermal for different fields would be obtained by tracing the points of intersection of a straight line carried parallel to itself with the curve of equation (1), the slope of the line being determined by the temperature.

For example, let a strong field be applied, then the intensity takes some high value F (fig. 3); as the field is reduced to zero, by the straight line through F being moved parallel to itself until it passes through the origin, the intensity falls to D . The point D gives the residual intensity of magnetization. Let the field now be carried to increasing negative values, which means that the straight line must be moved

parallel to itself on the other side of the origin. When this is done the line at some point C becomes tangent to the curve, and if there were any further growth of the negative field the line and the curve would part company and there would be no positive value of I which would satisfy both equations; the magnetic intensity then enters an unstable region. But since I can take negative as well as positive values the curve of equation (1) must be continued symmetrically in the opposite quadrant, as in the figure, and it is then seen that when the straight line parts company with the curve of positive values of I it is cutting the negative branch of the curve at F' , where there is a stable negative value for I . Thus, at the point C, the magnetization becomes unstable and rapidly passes over to the point F' on the negative side, and for increasing negative fields it continues along the stable path $F'R'$.

Again, as the field is carried from negative to positive values, the intensity passes from a high negative value through its residual value at D' to the point of instability C' , and then suddenly changes to a positive intensity at F .

Hence, when the field performs a cyclic change from positive to negative and back to positive values, the magnetic intensity traces out a hysteresis loop. A part of this loop is represented for the reduced temperature $\frac{T}{T_c} = 0.3$ in the upper part of fig. 4, where the negative field is given on an arbitrary scale.

4. Expressions can be obtained for (a) the reduced residual magnetic intensity at the point D, (b) the reduced intensity at the point of instability C, and (c) the negative field which gives rise to instability. Let the values of (a), (b), and (c) be put m_r , m_u , and H_u respectively where

$$m_r = I_r/I_0 \quad \text{and} \quad m_u = I_u/I_0.$$

If $m = I/I_0$ equations (1) and (3) are

$$m = \coth x - \frac{1}{x}, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$m = \frac{R}{\mu N I_0} T x - \frac{H}{N I_0} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

(a) When $H=0$ m_r is at once determined as the intersection of (4) and (5) for the given temperature T .

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(b) The tangent to the curve of equation (4) at any point is

$$\frac{dm}{dx} = \frac{1}{x^2} - \frac{1}{\sin h^2 x}, \quad (6)$$

and this must be put equal to the coefficient of x in equation (5), hence

$$\frac{1}{x_u^2} - \frac{1}{\sin h^2 x_u} = \frac{R}{\mu N I_0} T, \quad (7)$$

where x_u is the value of x for instability. When T is chosen x_u is thus determined, and x_u being known, m_u is found from equation (4).

(c) The field for instability (H_u) is the value of H in equation (5) when the reduced intensity is m_u ; thus

$$H_u = \frac{R}{\mu} T x_u - m_u N I_0 (8)$$

or

$$H_u = \frac{R}{\mu} T x - N I_0 \left(\coth x_u - \frac{1}{x_u} \right), \quad (9)$$

and H_u is thus determined when T is given and x_u found. If T is less than the critical temperature then the first term is less than the second and H_u is negative.

(5) We can trace the variation with temperature of this field for instability by plotting H_u , the intercept which the line tangent to the curve cuts off from the vertical axis against the tangent of the inclination of the line as it varies with the temperature. When this is done we get the curve traced in the inset to figure 4, plotted to arbitrary scales, and it is seen to be like the one found for the variation of these two quantities as deduced from the ferromagnetic equation. The remarks made in reference to that curve apply in the same way here.

(6) As both the ferromagnetic equation and the kinetic theory have been developed in a general manner, it follows that all ferromagnetic bodies should conform to the theory of corresponding states both for $I=f(T)$ and for $I=\phi(H)$. There is evidence for the truth of this in the relations of residual magnetic intensity to temperature, but the proof is not yet complete that corresponding states hold in the relations of intensity to field-strength. Experiments on this subject are in progress as already mentioned.

(7) Weiss considers the critical temperature to be the temperature at which the straight line of equation (3) is tangent to the curve $m = \coth x - \frac{1}{x}$ at the *origin*, and hence the intensity ought to fall to zero at the critical temperature. This is only true for residual magnetism when there is no external field in action. But if there is an external field in action the intensity does not, in fact, become zero at the critical point, but diminishes asymptotically, and apparently an infinitely high temperature would be required to annul the intensity altogether. Weiss meets this latter case by supposing that at some very low value of I , H becomes comparable with NI and is no longer negligible in the equation

$$x = \frac{\mu(H + NI)}{RT},$$

and then the theoretical relation of I to T above the critical temperature has the appropriate hyperbolic shape. The theory in its present form, however, does not lead to a definite point where the intensity and field have critical values, and the temperature which has been treated as the critical temperature is really the temperature of disappearance of magnetism when the field is zero.

III.

1. The relation of magnetic intensity to field-strength has been treated so far in a general manner and without the introduction of specific values. It remains to give numerical values to the constants and to compare the results with experimental facts. The expressions for the critical constants from the ferromagnetic equation are

$$T_c = \frac{8}{27} \frac{a'I_0}{R'}; \quad I_c = \frac{1}{3} I_0; \quad H_c = \frac{1}{27} a' I_0^2.$$

From the equation to the critical temperature a value for a' has been derived*, and by using this value the intrinsic field and the critical field can be calculated. Accepting the values of a' derived from the critical temperature, we find

$H_c = 0.82 \times 10^6$ for iron, and $H_c = 0.89 \times 10^6$ for nickel.

If, however, curves of $I = \phi(H)$ are consulted the critical fields for these metals appear to be less than unity. In the same way calculated values for the field for instability and

* Ashworth, Phil. Mag. vol. xxx. p. 723 (Nov. 1915).

the field-coefficient (α_H), which are closely connected with the critical field, differ from what are observed by a factor of the order 10^6 .

(2) In seeking to resolve this apparent discord between theory and experiment, the following considerations must be kept in view.

The intensity of magnetization, unlike the density of a fluid, is a vector quantity. Thus zero intensity does not necessarily imply the absence of an intrinsic field as zero density would imply the absence of an intrinsic pressure.

With ferromagnetics below the critical temperature zero intensity means that the orientation of the molecular magnets is such that the resultant field for points outside the magnet vanishes; the intermolecular field or intrinsic field is still existing and its magnitude may be not very different from what it is under a high intensity of magnetization.

If magnetization is regarded as the orientation into more or less complete alignment of molecular magnets moving in an intrinsic field, the action of an externally applied field must be mainly a directive one. For example, it is a familiar fact that an external field of a few units leads to very high inductions, and, on the other hand, very high inductions (of as much as 16,000 lines of force per sq. cm.) are easily annulled by a reversed field of a few units. It is evident in the latter case that the external field does not counter-balance the induction, but only controls it directionally.

The external field, when applied to an unmagnetized ferromagnetic, may be imagined as acting immediately on a few of the molecular magnets, which are more easily affected than the majority, and these act on neighbouring molecules which in their turn re-act on others, and so the effect of the initial stimulus rapidly spreads and an intensity of magnetization is produced which puts in evidence the intrinsic field. Thus a small external field does not create but may control a large intrinsic field*.

It was from this point of view that the statement was made that a latent heat of magnetization, if it exists, must be very small, since in magnetism the rapid acquirement of magnetic intensity only involves the orientation but not the creation of a magnetic intrinsic field, whereas in fluids the rapid condensation of a saturated vapour to liquid involves the creation

* The remarks here made apply equally well to the Kinetic theory. The intrinsic field given by Weiss as NI has a magnitude of the order 10^7 gauss, but it may be controlled by a small external field, and physically this small field is not to be neglected. The retention of the external field in the treatment of the Kinetic theory in Part II. is thus justifiable.

of an intrinsic pressure, and consequently there is a development of latent heat.

Where there is a destruction or creation of the magnetic intrinsic field, as there is by heat in the vicinity of the critical temperature, large thermal effects are to be expected such as have been found*.

3. An attempt may be made to determine the ratio (μ_i) of that part of the intrinsic field which is put in evidence (H_i) to the field (H) which is externally applied.

If H be very small compared to H_i , it may be numerically neglected and then the ferromagnetic equation becomes

$$H_i \left(\frac{1}{I} - \frac{1}{I_0} \right) = R'T$$

where R' is the paramagnetic constant. Also it has been previously shown that the equation to the anhysteretic isothermals,

$$H \left(\frac{1}{I} - \frac{1}{I_0} \right) = R_1 T,$$

is approximately true when R_1 is a constant†, hence by division we have

$$\frac{H_i}{H} = \frac{R'}{R_1}.$$

Now R' is the reciprocal of Curie's constant and has the value 3.56 for iron and 20.8 for nickel. An estimated value of R_1 deduced from some recent experiments, not yet published, is 0.77×10^{-6} for iron and 3.27×10^{-6} for nickel‡, when the maximum intensities are 1685 and 510 for these metals respectively, hence,

$$\mu_i = \frac{H_i}{H} = \frac{R'}{R_1} = 4.6 \times 10^6 \text{ for iron and } 6.4 \times 10^6 \text{ for nickel.}$$

4. Using this ratio the external critical field (H_{ec}) which corresponds to the critical field (H_c) is $H_{ec} = H_c / \mu_i$, and therefore, inserting numerical values, $H_{ec} = 0.18$ for iron and 0.14 for nickel.

From the value for the critical field the external field

* Hopkinson, Phil. Trans. Roy. Soc. A. 1889, p. 443; Honda, Sci. Reports, Sendai, Japan, vol. ii. no. 2 (1913).

† Phil. Mag. xxvii., Feb. 1914.

‡ These numbers are derived from curves of $I = \phi(H)$ constructed from curves of $I = f(T)$ in which hysteresis was suppressed by heating above the critical temperature, readings being taken as the metal cooled.

for instability (H_{eu}) at air temperature can be calculated thus :—

$$H_{eu} = -l_u \times H_{ec},$$

$$H_{eu} = -8.1 \times 0.18 = -1.4 \text{ for iron, and}$$

$$H_{eu} = -4.9 \times 0.14 = -0.7 \text{ for nickel.}$$

If the magnetic intensity fell abruptly at the field for instability this field would be the coercive field at the given temperature. In well-annealed pure iron the magnetic intensity falls very sharply as a nearly vertical line on a hysteresis diagram of $I = \phi(H)$, and consequently, -1.4 , the external field for instability, is approximately the coercive field as found by experiment. In nickel, however, the intensity falls sluggishly, the magnetism behaving like a viscous fluid, and therefore the field for instability cannot be compared with the experimentally determined coercive field.

5. In this and the previous paper on this subject* it has been shown that Curie's paramagnetic law of magnetism may be extended to include ferromagnetism in the same way as the gas law may be extended to include the behaviour of a liquid. The ferromagnetic equation which is analogous to Van der Waals's equation to fluids recognizes two salient facts in magnetism, namely, a limit to the magnetic intensity and the existence of an intrinsic field. The existence of such a field cannot be denied, but its calculated value is so large that it calls for some remarks.

The magnitude of the intrinsic field is derived mainly from thermal considerations. It is based on the value of α' , the intrinsic constant, which has been obtained from the equation to the critical temperature (T_c), where

$$T_c = \frac{8}{27} \frac{\alpha' I_0}{R'}.$$

Now T_c and I_0 are known with considerable accuracy, and the experimental value assigned to R' cannot be seriously in error. It may, indeed, be calculated from the gas constant and the maximum intensity in the following way.

The paramagnetic equation

$$\frac{H}{I} = R'T \text{ or } \frac{1}{K} = R'T$$

is a susceptibility equation, but it may be converted into an energy equation by multiplying both sides by $\frac{1}{2} I_0^2$.

* Ashworth, *loc. cit.*

The thermal energy may be written RT , hence

$$\frac{1}{2}I_0^2 R' T = RT, \text{ or } R' = \frac{2R}{I_0^2},$$

where R is the gas constant. When R' is calculated in this way for iron, nickel, and cobalt, it is found to be in sufficiently good agreement with experimental values to show that it may be safely used in determining a' , and hence in determining the magnitude of the intrinsic field ($a'I_0^2$) which is thus found to be about 10^7 gaussess.

There is another consideration which may be cited in this connexion. A ferromagnetic substance above the critical temperature behaves as a paramagnetic body, and the intensity of magnetization is directly proportional to the field-strength. Let a field now be applied, if possible of 10^7 gaussess, then the susceptibility being constant the intensity will become as great as the maximum in the ferromagnetic state. If, now, the temperature be lowered below the critical temperature, the field still being in action, no change occurs in the intensity, but the substance has changed from the paramagnetic to the ferromagnetic state, and that without any abrupt transition. According to this argument the two states are continuous and the magnitude of the ferromagnetic field is of the order of 10^7 gaussess.

Again, the progressive increase of the specific heat of a ferromagnetic substance as it is heated up to the critical temperature, when a sudden diminution occurs, is quantitatively accounted for with a high degree of accuracy by the gradual loss and final destruction of a field of the order of 10^7 gaussess*. Thus thermal considerations lead to the conclusion that the intrinsic field is of enormous magnitude. This conclusion is borne out also by the results of an electrolytic experiment on the electromotive force of magnetization to which I have referred in a former paper †.

On the other hand, if this intrinsic field is a *uniform* one and of magnetic origin, then only a small fraction of its lines of force are observable on the outside of the magnetized body, and, moreover, there are difficulties in accounting for the source of so large a field if the molecular specific magnetism is of the same order as that of the whole mass at its maximum.

For the present, therefore, it may be left an open question

* Weiss & Beck, *J. de Phys.* ser. 4, t. 7. p. 249 (1908).

† Ashworth, *Phil. Mag.* vol. xxx. p. 713 (1915); *Mem. & Proc. Manchester Lit. & Phil. Soc.* vol. lvi. part ii. (1914).

whether this intrinsic field is to be treated as altogether a true magnetic field, or if it is in part due to other than magnetic forces which are in operation and which, playing the part of magnetic forces, have been evaluated in terms of a magnetic field.

In conclusion, the ferromagnetic equation does not claim to be a complete statement of the complex facts of magnetism, but rather is to be regarded as a limiting law to which ferromagnetic substances tend to conform when the molecular magnets are free to move under thermal agitation with no other constraints than the external field and the intrinsic field, just as the paramagnetic equation is a limiting law to which paramagnetic substances tend to conform when the molecular magnets are free to move under thermal agitation with no other constraints than the externally applied field.

XXXIII. *On Discontinuous Wave-Motion.*—Part III.
By C. V. RAMAN, M.A., and ASHUTOSH DEY *.

[Plate VIII.]

IN a previous communication under the same title published in this Journal (Phil. Mag. Jan. 1916), it has been shown that by imposing a linear distribution of initial velocities with a discontinuity at one end upon a stretched string in its position of equilibrium, free oscillations may be obtained of identically the same type as the principal mode of vibration of a bowed string. The experiment furnishes a striking confirmation of the analytical theory of the motion of bowed strings. In the present paper it will be shown that some of the more complicated types of vibration of a bowed string may also be investigated by similar methods. Figs. 1 and 2 (Plate VIII.) reproduce a few typical records from amongst those secured in the course of this work.

From the mechanical theory, it appears that the most general form of vibration of a bowed string obtained by applying the bow at a point *not* coinciding with any node of importance approaches *in the limit* a type defined by one, two, three, or more *equal* discontinuous changes of velocity travelling over it. But when the limiting conditions are not attained, the mode of vibration may still to a close approximation be defined by a finite number of such discontinuous changes of velocity, these no longer being all equal to one another or of the same sign. In the present paper we

* Communicated by the Authors.

are concerned only with the cases in which *two* discontinuous changes having the same sign define the form of vibration. These cases may be considered in two broad divisions, the first comprising the limiting types in which the two discontinuities are of the same magnitude and sign; and the second, those in which they are unequal. We may discuss these separately.

Two Equal Discontinuities.

In this case the velocity-diagram of the string must evidently consist of three parallel straight lines, each passing through one of the three nodes of the second harmonic, namely, the two ends of the string and its centre. At particular epochs, however—that is, when the discontinuities pass each other or reach an end of the string,—one or even two of the straight lines may contract and vanish, leaving only two lines or one line on the diagram. For instance, if the two discontinuities are at the two ends of the string simultaneously, the diagram reduces to one line passing through the centre of the string. As the discontinuities move in towards the centre, two new lines appear, each passing through an end of the string, and the third line passing through the centre gradually contracts and finally vanishes when the discontinuities both arrive and pass each other at the centre. The line then reappears and the form of the velocity-diagram then goes back to its initial state, passing through the same stages in the reverse order. It is obvious that in this case the centre of the string remains completely at rest, and that the string vibrates in two segments with double the ordinary frequency, the fundamental component being entirely absent. In general, however, the discontinuities do not cross at the centre of the string, but at some other point; if one such crossing takes place at a point distant $l/2 + b$ from an end (l being the length of the string), a second crossing would take place half a period later at the point $l/2 - b$. The vibration-curve at either of the points $l/2 \pm b$ is readily seen to be a simple two-step zigzag. For, the velocity of either point remains unaltered when the two discontinuities pass over it simultaneously in opposite directions, and changes only at the two epochs at which either discontinuity passes over it *singly*. If $\tan \alpha$ be the slope of the lines of the velocity-diagram, the velocity at either point changes at the first epoch from $b \tan \alpha$ to $(l/2 - b) \tan \alpha$, and changes back again to its original value at the second epoch. The fraction of the total period of vibration during which the larger velocity subsists is given by the ratio $b/2l$, or by

the ratio $(l-2b)/l$, according as b is smaller or greater than $l/4$.

The form of the vibration-curve at other points on the string in the case considered above may also be found by tracing the successive changes of velocity. It is obvious that the curves for points lying outside the limits $l/2 \pm b$ are different in character from those for points lying between these limits. For, the discontinuities pass any point lying outside the limits $l/2 \pm b$ alternately in opposite directions, so that the velocity of such point alternates between two, and only two, constant values. But within those limits the discontinuities pass any given point, first successively in the same direction, and then successively in the opposite direction. The vibration-curves of points lying outside the limits $l/2 \pm b$ are four-step zigzags, in which alternate lines are parallel to each other. The vibration-curves of points within the limits $l/2 \pm b$ are also four-step zigzags, in which two of the lines are parallel to each other, but the other two are not. The most characteristic vibration-curve is that for the centre of the string. This point remains at rest for a considerable interval, twice in each period of vibration, the two positions of rest lying one on either side of the undisturbed position of the string. The smaller the distance b is, the more closely are the two positions of the centre of the string situated. The vibration-curve of the middle point of the string thus consists of two long horizontal lines which take up a considerable fraction of the period of vibration, and are separated by short steep lines representing the motion from one position of rest to the other, and *vice versa*.

Experimental Method.

It is evident that the modes of vibration described above would be perfectly reproduced if a string has initially a uniform angular velocity about one point, and if in the course of this motion two other points on it situated at equal distances on either side of the first are suddenly fixed with the result of isolating the string between them. If A and B are the points thus fixed and C is the point about which the string has initially a uniform angular velocity, so that $AC=CB$, the mode of vibration elicited would evidently depend upon the simultaneity, or otherwise, of the fixation of the string at A and B. If the two points are fixed at the same instant, the discontinuous changes of velocity travelling inwards from A and B meet at the centre, and the string would, as already explained, vibrate in two segments. On the other

hand, if one of the points is fixed earlier than the other by an interval of less than half a period, the discontinuities cross at some point on the line A B other than the centre of the string, the position of such point being capable of adjustment by a suitable alteration of the interval of time between the fixing of the string at the points A and B.

The experiment here indicated may be successfully performed with a steel "string" stretched on a light frame capable of motion round a horizontal axis at right angles to it. The necessary tension is secured and maintained by a spring-balance fixed to one end of the frame, which keeps the string taut. A small load fixed to the frame on one side causes it to swing into a horizontal position with the angular velocity desired. At this position the string comes up against two stops, one on either side of it, situated at equal distances from the horizontal axis about which the frame and string move. If the two stops A and B are exactly in line with the string at this instant, the impacts take place simultaneously. By putting one of the stops out of line, any desired interval between the impacts may, however, be secured. It is found (with the arrangements adopted by us) that a vertical displacement of one of the stops by a millimetre is equivalent to about half a period in the interval between the impacts, smaller displacements securing proportionately smaller intervals. Just before the impacts take place, the dark slide containing the photographic paper is released automatically, and moves in a direction parallel to the string, recording the initial motion and the vibration of the string at any point desired. The optical arrangements are similar to those described in the first paper of the series.

Fig. 1 (Plate VIII.) shows eight records secured by these arrangements for various points on the string, and exhibits a complete agreement with the indications of theory. Two of the records (for $3l/8$ and $5l/8$) show a close approach to the simple two-step zigzag form for the point at which the discontinuities cross. The ratio of the two velocities of this point or of any other point lying outside the limits $l/2 \pm b$ is equal to the ratio of the distances of such point from the centre and the nearer end of the string. The photographs furnish a confirmation of this kinematical law. Numerous records (not published) have also been secured of the vibration-forms obtained for values of b ranging from zero to $l/2$. When $b=l/4$, the two sides of the two-step zigzag for the points $l/2 \pm b$ are equally steep, and a vibration of the type considered here cannot therefore be elicited by the bow with a two-step zigzag motion at the bowed point if $b > l/4$. As b

is increased from $l/4$ to $l/2$, the vibration-curve at every point on the string approaches the simple two-step zigzag form, and finally becomes identical with it.

Two Unequal Discontinuities.

By setting the axis of rotation of the frame elsewhere than at the point bisecting AB , the case of two unequal discontinuous changes of velocity may be realized experimentally. In this case, no line on the velocity-diagram passes through the centre of the string. If the discontinuities cross at the points $l/2 \pm b$, theory shows the vibration-curves for points outside these limits to be four-step zigzags, in which the two lines of small slope are parallel, but the other two lines are not parallel to each other. Between the limits $l/2 \pm b$ the vibration-curves are four-step zigzags in which none of the lines are parallel. If $b=0$, the vibration-curves are everywhere of a symmetrical type. Otherwise they are everywhere unsymmetrical. The vibration-curves at the points $l/2 \pm b$ consist of only three lines in each period unless $b=0$, in which case there are only two. The most interesting forms are those obtained at the centre of the string and those near an end.

Fig. 2 (Plate VIII.) shows some records obtained when the axis of rotation of the frame passed through a point of trisection of the length AB . Here again a complete agreement with theory is shown. Forms of vibration set up by two discontinuous changes of velocity may be obtained by bowing a string near one end with pressure insufficient to elicit a pre-eminent fundamental*. In this case the discontinuities are generally unequal, though in special cases they may approach or attain equality. Generally, the vibration-forms thus obtained are unsymmetrical; but they may closely approximate to the symmetrical types under favourable conditions †.

Summary and Conclusion.

By setting up two discontinuous changes of velocity, either simultaneously or in succession, upon a stretched string which has initially a uniform angular velocity,

* "On the Wolf-note in Bowed Stringed Instruments." By C. V. Raman, M.A. Phil. Mag. Oct. 1916.

† Some of the symmetrical stationary forms with two unequal discontinuities obtained by bowing were observed and figured by Helmholtz ('Sensations of Tone,' English Translation by Ellis, page 85). Helmholtz's drawing is, however, not quite correct, as the shorter descent should appear in the vibration-curve as less steep than the longer.

vibration-forms may be obtained which are identical with: (a) the motion of a string bowed with suitable pressure close to its centre, or at a distance from it not exceeding a quarter of its length; (b) the motion of a string bowed near an end with pressure insufficient to elicit the fundamental pre-eminent; and (c) the successive stages of the vibration obtained by bowing a string near an end at the "wolf-note" pitch, or under certain other circumstances in which *cyclical*, not periodic, vibrations are obtained.

The photographic records are in complete accord with theory, and are an interesting illustration of the experimental analysis of discontinuous vibration-forms.

The experiments described in this note were carried out in the Laboratory of the Indian Association for the Cultivation of Science.

Calcutta,
November 8th, 1916.

XXXIV. *Note on Prof. Anderson's "Focometry of Lens-Combinations."* By ROBERT E. BAYNES, M.A.*

PROF. ANDERSON'S method (p. 157) of determining the focal length of a combination is most interesting, but the degree of its exactness requires examination; for the data given in the paper for a particular case, viz. $x_1=51.0$, $y_1=9.0$, $x_2=24.5$, $y_2=9.5$, $d=26.9$, lead to curious results when treated in different ways.

Prof. Anderson's formula

$$f = d \div (x_1/y_1 - x_2/y_2)$$

gives $f=8.71$, but the distance between the nodal planes when calculated from this value of f with x_1, y_1 is 8.52 and with x_2, y_2 is 6.58, a difference which cannot be ignored.

The fact is that there is a definite relation between the five given magnitudes, viz.

$$d(1 - y_1 y_2 / x_1 x_2) = (x_1 - y_1) - (x_2 - y_2),$$

which is not satisfied in the above case and which requires $d=29.0$ with the given values of x_1, \dots With this value of d we should have obtained 9.39 for the focal length and 5.93 for the distance between the nodal planes.

* Communicated by the Author.

One would fancy that, of the measurements given above, those of $d=26.9$, $x_1-y_1=42.0$, $x_2-y_2=15.0$ might be taken as exact almost to a millimetre. Now the above formulæ lead to

$$f = d \div \{x_1/y_1 - d(y_1/x_1)\} / (d + x_2 - y_2 - x_1 + y_1) :$$

and if we take as exact the above given values of x_1 and y_1 with x_2-y_2 and d , we obtain 0.51 for the focal length and 1.95 for the distance between the nodal planes; whereas, if we assume as exact the given values of x_2 and y_2 with x_1-y_1 and d (in this case -26.9 , with interchange of the subscripts in the formula), we find -0.25 for the focal length and 15.1 for the distance between the nodal planes.

It would be interesting to know what is the exact focal length, found otherwise, of the combination in question and the exact reason of these most discrepant results. A method requiring the determination of only one centre of rotation together with two measurements that can easily be made with very fair accuracy would seem *a priori* to be more reliable than one requiring the determination of a second centre of rotation as well.

It may be noted that the point of rotation of the combination in any position is the intersection of its axis with the line joining a point and its image.

Christ Church, Oxford,
Feb. 16, 1917.

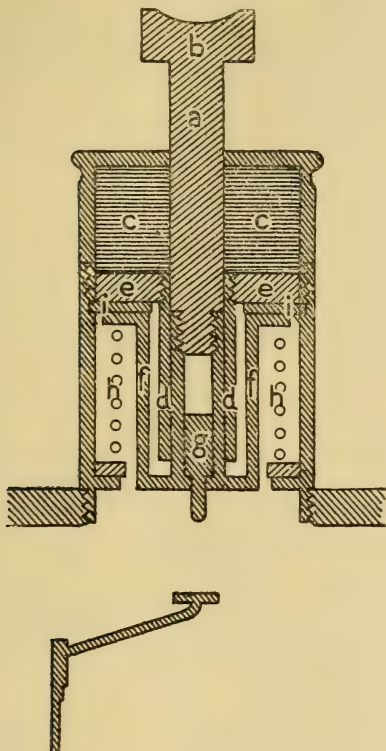
XXXV. *On an Automatic Device for charging Electroscopes.*

By L. KOLOWRAT, Assistant at the Mineralogical Laboratory, Imperial Academy of Sciences, Petrograd.*

HAVING had to construct a set of sensitive aluminium-leaf electroscopes for laboratory and field work with radioactive minerals, I have fitted them with a special charging device which, though somewhat elaborate in design, is simple and convenient in use, and may therefore deserve a few words of description. It consists essentially of an ebonite rod *a* which, whilst being pushed down by means of the button *b*, is rubbed against cloth placed at *c*, *e. g.*, in form of a pile of perforated disks. During the subsequent motion, the charge thus produced is collected on the fixed brass tube *d*, insulated by the ebonite collar *e*.

* Communicated by Sir E. Rutherford.

This tube remains, on the other hand, in permanent connexion with the piece *ff*, consisting of two coaxial cylinders and moved together with *a*. When the rod is at the end of its path, a small finger *g* lightly touches the support of the leaf to be charged. By releasing the pressure on *b*, the



spring *h* brings the rod to its original position, simultaneously connecting *f* with the brass disk *i*, and consequently with the electroscope-case. The dimensions being chosen consistent with the capacity of the leaf-support, things are easily adjusted so as to produce a convenient deflexion of the leaf with a single push of the button. A good plan is to overcharge the leaf a little and to keep the button down until the system has discharged itself to the desired point, which is readily attained owing to the leak through the ebonite parts of the charging device.

It is hoped that this device may prove useful not only in the laboratory but also for electroscopes in field-work.

Petrograd, Jan. 1917.

XXXVI. *A Polarization Flicker Photometer and some Data of Theoretical Bearing obtained with it.* By HERBERT E. IVES*.

Synopsis.

1. Introduction.
2. Theory and Construction of a Polarization Flicker Photometer.
3. Theory and Construction of a Mixture Photometer.
4. Critical Speed Relations for various relative Brightnesses of Two Compared Fields.
 - (a) Mean Brightness Constant.
 - (b) Mean Brightness Varied.
5. Measurement of the Brightness Difference Discrimination Fraction for Fluctuating Impressions.
6. Critical Speed Relations with a Difference of Colour between the Two Fields under Comparison.
7. Measurement of the Hue Difference Discrimination Fraction for Fluctuating Impressions.
8. Relative Values of Brightness and Hue Discrimination Fractions under Steady and Fluctuating Conditions.
9. Effect of Choice of Speed on Flicker Photometer Settings.
10. Summary.

1. *Introduction.*

IN previous papers by the present writer and Mr. E. F. Kingsbury on "The Theory of the Flicker Photometer" †, emphasis was laid on the desirability, from both the practical and theoretical sides, of a flicker photometer in which the transition from one field to the other should be gradual and according to some simple mathematic relation. Practically the advantage is in eliminating mechanical flicker, due to dividing edges, which can introduce spurious effects. Theoretically the advantage is that this kind of transition, especially if it can be represented by the simplest periodic function—the cosine curve—can be handled mathematically ‡.

The theory developed by us was based on a stimulus represented by a cosine curve. The verification of the theory by experiment, which was sought in work with flicker photometers with abrupt transition, while very satisfactory, was incomplete quantitatively in several details. We gave reasons for believing that the outstanding discrepancies were ascribable to the difference between the type of

* Communicated by the Author.

† "Theory of the Flicker Photometer," Ives & Kingsbury. *Phil. Mag.* Nov. 1914, p. 708; April 1916, p. 290.

‡ Other transitions can of course be represented mathematically; the difficulty is in solving the equations resulting when the diffusivity conditions are introduced.

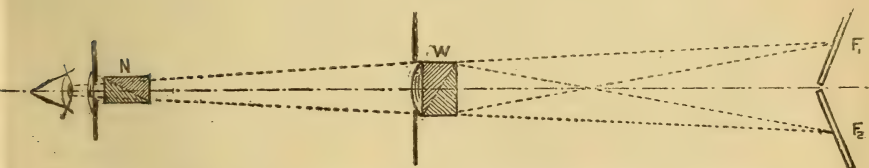
flicker photometer theoretically postulated and that actually used.

In the present paper a flicker photometer is described in which the transition from one light to another is exactly of the character handled in the theory. It has been possible with this photometer to verify accurately the predictions of the theory. Measurements of the visual constants have been made, and, as a consequence, the complete behaviour of this type of equal exposure flicker photometer can now be represented quantitatively by a set of equations derived from the physical theory of conduction.

2. *Theory and Construction of a Polarization Flicker Photometer.*

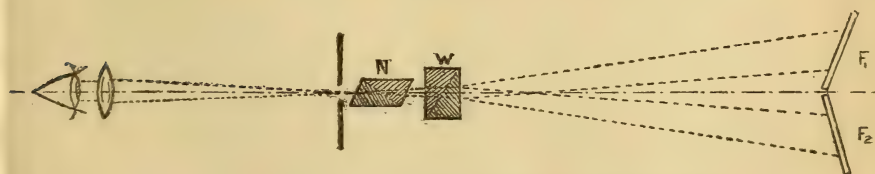
The polarization flicker photometer is a combination of a double-image prism with a rotating Nicol prism. Two images of each half of the photometric field are formed by the double-image prism, and the dimensions of the apparatus are so chosen that the horizontally polarized image of one half is superposed on the vertically polarized image of the other. The Nicol prism as it rotates alternately extinguishes each image, the one fading gradually into the other, with entire absence of any mechanical edge effect.

Fig. 1.



Polarization flicker photometer: N, rotating Nicol prism; W, double-image prism; F₁ and F₂, two halves of photometer field.

Fig. 2.



Alternative arrangement of polarization flicker photometer.

Figs. 1 and 2 show two constructions. In fig. 1 the Nicol prism is placed at the eye. When so used the nicol must be of the type in which the faces are perpendicular to the beam

of light, otherwise the whole field will oscillate with the rotation of the prism. In fig. 2 the nicol is placed away from the eye and beyond the diaphragm which limits the field. In this arrangement the nicol may be of the oblique-faced type. The apparatus actually used was arranged as in fig. 2, because of the kind of nicol prism available. The distances were such that the photometric field had an angular aperture of $1\frac{1}{2}$ degrees. The artificial pupillary aperture was 3 mm. in diameter.

The theory of the polarization flicker photometer is simple. Let $2I_0$ be the brightness of the image polarized in one plane, then the brightness of the image when the nicol is rotated through the angle ϕ from that plane is

$$2I_0 \cos^2 \phi.$$

Now $2I_0 \cos^2 \phi = I_0 (1 + \cos 2\phi) \quad . \quad . \quad . \quad (1)$

If we put $2\phi = \omega t$, the right-hand member of (1) becomes the right-hand member of equation (1) in the first theoretical paper, that is, we have exactly the type of stimulus there postulated.

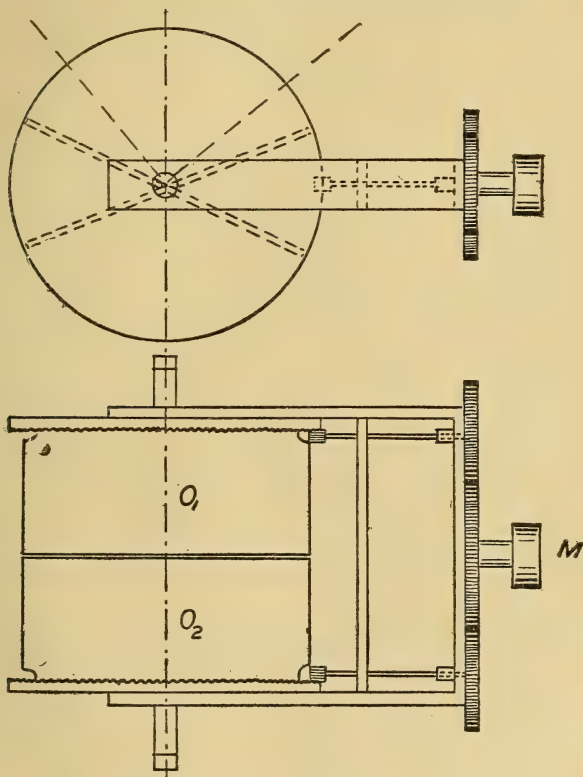
3. *Theory and Construction of a Mixture Photometer.*

In the discussion of colour flicker it was shown that the action of the flicker photometer is to form a mixture of the two colours under measurement. The speed at which it is necessary to run the flicker photometer in order that there shall be no colour flicker is that at which the hues of the extreme mixtures differ less than the least perceptible hue difference. The relationship of this hue difference to the least perceptible brightness difference and the relationship of both of these to the corresponding quantities for steadily viewed juxtaposed fields, are crucial points in flicker photometer theory.

In order to be prepared for hue difference perception measurements the photometer "head," if it may be so called, was made in such a way that the light from the two sources under comparison could be mixed in any desired proportions. The apparatus is shown diagrammatically in fig. 3. It consists of two translucent (flashed opal) glasses, arranged, one over the other, to turn by means of gears in opposite directions, about a common axis parallel to their faces. This device is set up at the intersection of two photometer tracks, standing at right angles to each other, and is viewed from the rear. If used for equality of brightness observations a biprism is employed to juxtapose images of the

two glasses. If used with the polarization apparatus the divergence of the double-image prism-beams easily clears the gap between glasses. A thin metal screen is placed in this gap to prevent illumination of one glass by the other, and the edges of the glasses are coated with opaque black paint.

Fig. 3.

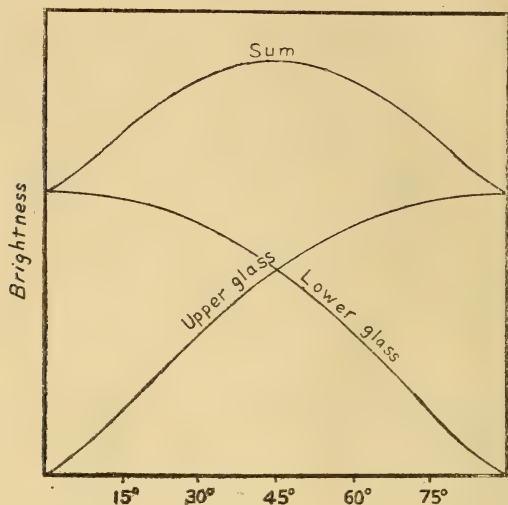


Mixture photometer: O_1 and O_2 are opal glasses turned in opposite directions by the milled head M .

With the glasses turned at right angles to each other and normal to the two photometer tracks the two glasses form the two halves of an ordinary equality photometer field. When turned at other angles various mixtures of the two lights are obtained. The brightness of each glass at various angles due to illumination by each light alone was carefully determined by measurements with a portable photometer. In

fig. 4 is exhibited the brightness of each glass due to illumination by a light source on one track alone, as the glasses are rotated. The *sum* of the two is calculated in order to facilitate moving the light sources, so that the *mean* brightness of the two glasses may be maintained constant as their *relative* values are changed by their rotation.

Fig. 4.



Relative brightness of upper and lower glasses of mixture photometer due to a single light source, for various angles of incidence of light on lower glass.

Using one light source, this device permits the comparison of fields of all degrees of relative brightness, but of the same colour. Using two light sources of different colour, but the same intensity, the device makes possible the comparison of fields of all hues intermediate between the two, formed by their mixture.

As a precautionary measure, the light transmitted by the two opal glasses was tested for any difference in polarization which would affect the setting of the polarization flicker photometer, but nothing of the sort was found.

4. Critical Speed Relations for various relative Brightnesses of Two Compared Fields.

(a) Mean Brightness Constant.

In the second of the papers on the theory the following equation is derived for the critical speed of disappearance of

flicker between two fields of unequal brightness:

$$\omega = \frac{2 \left[\log \frac{2}{\delta} + \log \frac{I_1 - I_2}{I_1 + I_2} \right]^2}{\frac{X^2}{K} (\log e)^2}, \quad \dots \quad (2)$$

where ω = critical speed,
 δ = brightness discrimination fraction,
 I_1 and I_2 = brightness of the two fields,
 K = diffusivity,
 X = depth of penetration.

If we assume that K is a function of the *mean* brightness, we can, by holding the latter constant as I_1 and I_2 are varied relatively to each other, make a test of the theory, in so far as it assumes a diffusivity apart from any question as to how this varies with intensity. Fig. 1 of the paper referred to shows critical frequencies for various values of I_1 and I_2 under these conditions, which were not attainable experimentally with the apparatus then available.

With the new apparatus just described the exact conditions for this test are met. In fig. 5 are shown the results of two extended sets of measurements of critical speeds for varying ratios of two fields, with the mean brightness held constant. The upper points were obtained at a relatively high, the others at a relatively low, illumination. The full lines are graphs of the equation (2), with a value δ of .001, using the values of $\frac{X^2}{K}$ solved for from the end points. It is clear that the theory is very beautifully borne out.

(b) Mean Brightness Varied.

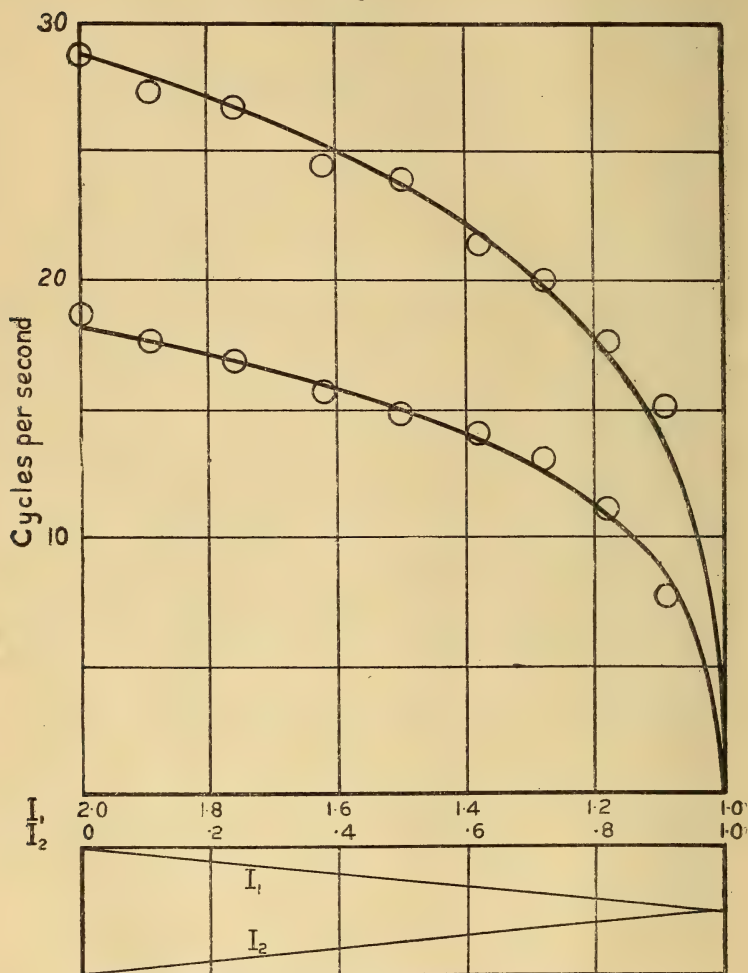
The second theoretical paper gives in equation (6) a relation for the critical speeds at different illuminations, which upon inserting the complete expressions for the constants becomes

$$\omega = \frac{\left[\log \frac{2}{\delta} + \log \frac{I_1 - I_2}{I_1 + I_2} \right]^2}{\left(\log \frac{2}{\delta} \right)^2} (a \log I_A + b), \quad \dots \quad (3)$$

where I_A is the mean brightness, and a and b are the constants (as determined by experiment) applying to the limiting case of light alternated against darkness. It follows from this equation that, critical speeds for the limiting case being

represented by a straight line when plotted against the logarithm of the intensity, critical speeds for other ratios of the fields should plot as straight lines lying below and

Fig. 5.

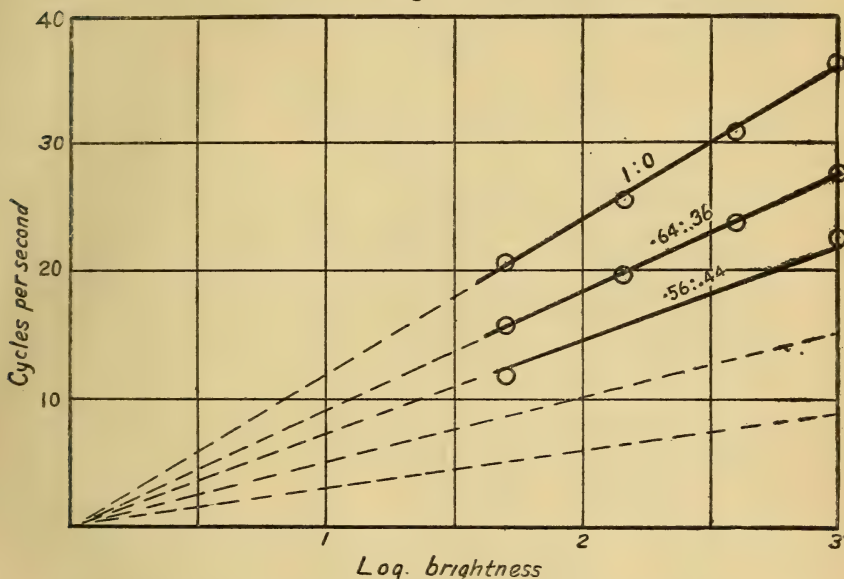


Critical frequencies for various ratios of brightness of two compared fields. Full lines, calculated curves for $\log \delta_B = -3.0$.

inclined to this at such angles that all will meet at a point on the axis of abscissæ. In our previous experimental work we did not get satisfactory confirmation of this equation.

Fig. 6 shows experimental values obtained to test the equation, using the new photometer. It will be seen that the theory is fully confirmed. Equation (3) is hence the *general expression*, of which the relation for light against darkness ($I_2=0$), as found by Porter, is a special case.

Fig. 6



Critical speed brightness relations for various ratios of brightness of two fields.

The value of δ called for by these data is about .0001, which is much smaller than the figure fitting the data of the previous section. The measurement of δ and its characteristic of variability call for separate discussion.

5. Measurement of the Brightness Difference Discrimination Fraction for Fluctuating Impressions.

A determination of the critical speeds for two different ratios of the fields furnishes all the necessary data for finding the value of δ .

Denoting the two different critical speeds and brightness ratios by the subscripts a and b , we obtain from (3)

$$\log \delta = \log 2 - \frac{\log \left(\frac{I_1 - I_2}{I_1 + I_2} \right)_a - \sqrt{\frac{\omega_a}{\omega_b}} \log \left(\frac{I_1 - I_2}{I_1 + I_2} \right)_b}{\sqrt{\frac{\omega_a}{\omega_b}} - 1}. \quad (4)$$

If for one of the brightness ratios is taken that of light against darkness the corresponding logarithmic term drops out, being zero. Measurements of the critical speeds for the ratios 1:0 and .34:.66 were made by the writer on several different occasions during the work, each consisting of four to six alternated series of ten settings each, from which the following values of $\log \delta$ were found:—

$$\begin{aligned}\log \delta &= -3.0 \\ &-4.2 \\ &-3.7 \\ &-4.2 \\ &-5.0\end{aligned}$$

These figures, all obtained for the same mean brightness, show that δ varies over quite wide limits, for these variations represent rather bigger differences in the critical speed ratios than can be ascribed to the lack of precision of the determinations, considerable though this is. There is clear indication of a progressive decrease in δ during the progress of the work.

In order to secure additional light on this point, similar measurements were secured from other observers who had not been working with the apparatus.

Their results are as follows:—

$$\begin{aligned}\log \delta &= -4.2 \text{ (E. K.)} \\ &-3.0 \text{ (E. F. K.)} \\ &-3.2 \text{ (E. F. K.)} \\ &-3.2 \text{ (E. R. M.)}\end{aligned} \left. \vphantom{\begin{aligned}\log \delta &= -4.2 \text{ (E. K.)} \\ &-3.0 \text{ (E. F. K.)} \\ &-3.2 \text{ (E. F. K.)} \\ &-3.2 \text{ (E. R. M.)}\end{aligned}} \right\} \text{several days apart,}$$

indicating that the fraction varies from individual to individual, as well as from time to time with any one observer.

The mean value of all these determinations is

$$\log \delta = -3.74 \quad \text{or} \quad \delta = .00018.$$

Remembering that the Fechner fraction, as ordinarily understood and determined for juxtaposed fields, is of the order of magnitude of 1 per cent., this value of δ appears extraordinarily low. It is well known, however, that the greatest sensibility to small brightness difference is obtained when the compared fields are most closely juxtaposed, but even then the comparison must be made between impressions received by different retinal elements. In the case of successive impressions the comparison is made of impressions on the same element, and there is nothing inherently improbable in the sensibility to such impressions being higher than the greatest sensibility attainable by juxtaposition. It

is to be noted, however, that this high sensibility, located as it is in the ultimate receiving apparatus, can never be utilized to its full value for the detection of small fluctuations in the stimulus. Because of the damping effect of the channel through which the impression of the fluctuating stimulus is transmitted, only very considerable fluctuations retain any amplitude large enough to be detected. In other words, the very small value of the brightness discrimination fraction of the ultimate receiver for successive impressions is all that makes possible our appreciation of ordinary fluctuations in the stimulus. If this had the value of the ordinary Fechner fraction we could tolerate much lower frequencies of light fluctuation than we now do. On the other hand, if we could stimulate the ultimate receiver directly, without the interposition of the present transmitting channel, it would be necessary to use rather high speeds of alternation to make flicker vanish. Upon substituting different values of δ in equation (4) of the second paper on the theory, the effect on ω is given numerically. A value of $\cdot 01$ for δ in place of $\cdot 00018$ about halves the critical speed.

6. *Critical Speed Relations with a Difference of Colour between the Two Fields under Comparison.*

It follows from the treatment, in the two theoretical papers, of colour flicker and of brightness flicker with unequally bright fields, that critical speeds should follow the same law in the case of two coloured fields as with two unequally bright fields, up to the point of the appearance of colour flicker. The latter interposes a bar to the progressive decrease of speed to zero which occurs at the equal brightness point for fields of the same colour. Detailed discussion of the statement just made may be avoided by reference to the diagrammatic insert to fig. 7. Here the two fields under comparison are supposed to be of different colour. The left-hand end of the figure represents the condition with one colour field alone exposed, and, as indicated below the larger figure, the brightness of this field is progressively decreased while the other field is increased in such manner that their sum remains constant. All points below the two critical frequency curves are in the region of brightness flicker. The curve which is drawn convex upward, with its maximum at the equal brightness point, is taken from the first theoretical paper and is the upper limit to the colour flicker region, or region in which the hue difference for successive phases of the flicker photometer is greater than the least perceptible.

No setting can be made at a lower speed than that fixed by the intersection of these curves. The actual observation of a flicker-limit curve such as that indicated by the small diagram, with its very definite truncation of the brightness flicker curves, should constitute a strong argument for the correctness of the line of reasoning followed.

For the experimental test of these relations, red and green lights were taken as furnished by two point source 100 watt tungsten lamps shining through red and green glasses of fairly narrow spectral transmissions. The two lamps were operated in parallel, one terminal of each going to the battery, the other terminals being connected to the opposite ends of a resistance, the sliding middle point of which was joined to the other battery terminal. By moving the sliding contact the intensity of one lamp increased while the other decreased, and *vice versa*, this constituting the best way of operating a flicker photometer, as previously pointed out. The first operation in this experiment consisted in finding, by the flicker photometer criterion, the equal brightness voltages for the lamps through their coloured glasses, each illuminating one of the opal glasses, placed normal to it, and these voltages were used throughout the work with them.

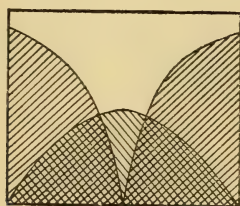
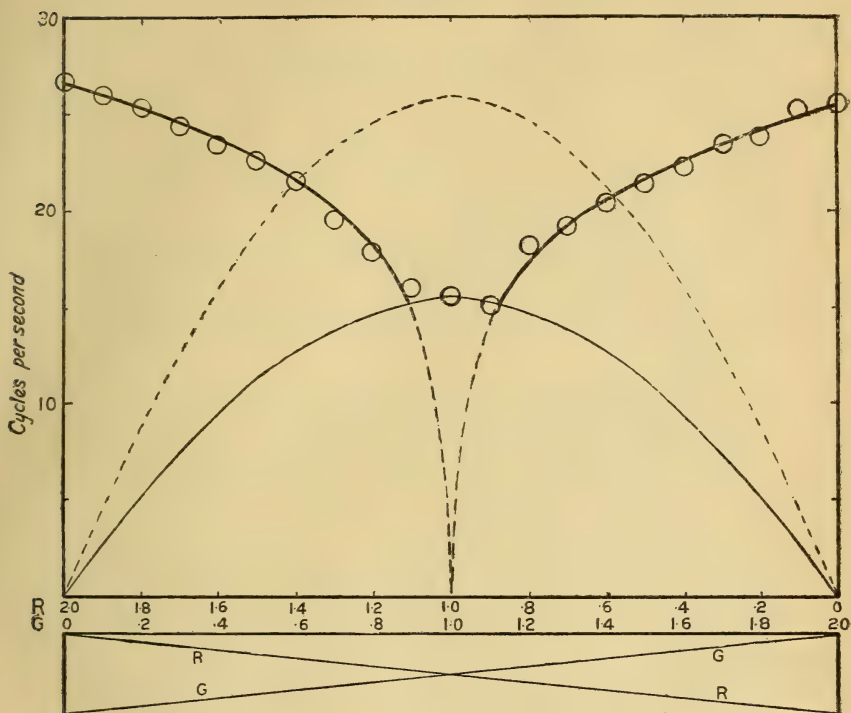
In fig. 7 are shown the critical frequencies obtained on carrying through the entire series of comparisons of the two coloured fields, the various relative intensities being obtained by moving the two lamps to various calculated positions on the photometer bar. It will be seen that the points follow the curves calculated from equation (2), ($\delta = .0002$) right down to the sharp intersection of the colour flicker limiting curve and then follow this across from one brightness flicker limiting curve to the other. As they should be, the critical frequencies at the end points are not exactly the same for two coloured lights equal by the flicker photometer criterion. The experimentally found relationships are in every respect in agreement with those indicated by the theory.

7. *Measurement of the Hue Difference Discrimination Fraction for Fluctuating Impressions.*

Exact determination of the speed at which colour flicker appears, which is made possible by the new flicker photometer, opens the way to the measurement of the just perceptible hue difference corresponding to the brightness difference fraction discussed in section 5.

In the first theoretical paper it is shown in equation (9) and its discussion, that if two coloured fields R and G of

Fig. 7.



Brightness flicker



Color flicker



Critical speed relations with a difference of colour between the two fields. Lower, diagrammatic; upper, experimental. Upper dashed curve, limit of colour flicker region if fluctuating hue discrimination fraction maintained its steady observation ratio to brightness discrimination fraction.

equal brightness are alternated in the flicker photometer, the ratio of R to G at one extreme phase is given by

$$\frac{R}{G} = \frac{\left(1 + e^{-\frac{X}{\sqrt{2K_1}}\sqrt{\omega}}\right)}{\left(1 - e^{-\frac{X}{\sqrt{2K_2}}\sqrt{\omega}}\right)} \cdot \cdot \cdot \cdot \cdot \quad (5)$$

and at the other phase by the similar expression with the + and - signs interchanged.

Before detailed discussion of this it is desirable to digress in order to develop the idea of a *hue scale* by which a numerical value can be given to any hue, and in particular the idea of a hue discrimination fraction will be developed and used.

Let us imagine the two juxtaposed fields of the mixture photometer illuminated by two equally bright but differently coloured light sources R and G. When the two opal glasses stand at right angles to each other and normal to each light source they are of the colour of these latter, and show their maximum colour difference. As they are turned towards parallelism they are illuminated by mixtures of the two colours and become progressively more like in hue, until at the position of exact parallelism they are the same. On turning further they diverge in hue until at the end position they show the same difference as at first, but in the opposite direction. Now if we consider these hues as forming a continuous series, they may be described and given a numerical value in terms of the proportion of one of the end colours present in the mixture forming any hue. If, for instance, we identify the hue by the amount of R in it, we have that the hue, H , of the mixture in which the two colours are present in the ratio $R_H : G_H$ is

$$\frac{R_H}{R_H + G_H}.$$

A hue difference $H_1 - H_2$ is then

$$\frac{R_{H_1}}{R_{H_1} + G_{H_1}} - \frac{R_{H_2}}{R_{H_2} + G_{H_2}}, \quad \cdot \cdot \cdot \cdot \cdot \quad (6)$$

and this is the fractional difference

$$\frac{H_1 - H_2}{\frac{H_1 + H_2}{2}} \cdot \cdot \cdot \cdot \cdot \quad (7)$$

If this hue difference is the least perceptible one, then we define the *hue difference discrimination fraction* by relation (7). We shall use the symbol δ_H for this fraction. It will be noted that this definition is exactly parallel to the definition of the brightness discrimination fraction, which is

$$\frac{I_1 - I_2}{\frac{I_1 + I_2}{2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

This will be symbolized by δ_B henceforth, to avoid confusion.

Applying now (6) and (7) to (5), we have that the hue at one phase is

$$H_1 = \frac{1 + e^{-\frac{X_1}{\sqrt{2K_1}}\sqrt{\omega}}}{2} ;$$

at the other phase it is

$$H_2 = \frac{1 - e^{-\frac{X}{\sqrt{2K_2}}\sqrt{\omega}}}{2} ;$$

from which

$$\delta_H = \frac{H_1 - H_2}{\frac{H_1 + H_2}{2}} = \frac{i \left[e^{-\frac{X\sqrt{\omega}}{\sqrt{2K_1}}} + e^{-\frac{X\sqrt{\omega}}{\sqrt{2K_2}}} \right]}{2 + e^{-\frac{X\sqrt{\omega}}{\sqrt{2K_1}}} - e^{-\frac{X\sqrt{\omega}}{\sqrt{2K_2}}}} \quad . \quad . \quad . \quad (9)$$

In order to handle this expression we may, as a close approximation, take K_1 equal to K_2 , defining it in terms of the mean of the critical speeds of the two colours, $\frac{\omega_R + \omega_G}{2}$, by the relation

$$\frac{\sqrt{2K}}{X} = \frac{\sqrt{\frac{\omega_R + \omega_G}{2} \log e}}{\log \frac{2}{\delta_B}} \quad . \quad . \quad . \quad (10)$$

We get then finally

$$\log \delta_H = \log 2 - \sqrt{\frac{2\omega_M}{\omega_R + \omega_G}} \log \frac{2}{\delta_B} \quad . \quad . \quad (11)$$

ω_M being the critical speed for the equality point*. Calculation of δ_H therefore presupposes a knowledge of δ_B , and any error or variation in δ_B will be reflected in the value found for δ_H †. It must not be overlooked that while the brightness difference discrimination fraction has only one value, the hue fraction is a function of the colour difference constituting the ends of the scale; the larger the colour difference the smaller will this fraction be.

Experimental values of δ_H for the red-green comparison used in this test are given in the next section.

8. *Relative Values of Brightness and Hue Discrimination Fractions under Steady and Fluctuating Conditions.*

The question of crucial importance in the flicker photometer is not so much the actual values of the discriminating fractions, but whether their *ratio* is different for fluctuating and steady conditions. If this ratio is the same, then the mixture by rapid alternation possesses no advantage over any other form of mixture photometer, in which each field is diluted with light from the other until the colour difference is no longer troublesome.

In order to examine these ratios for both steady and fluctuating conditions, it was necessary to arrange for the measurement of both discrimination fractions with juxtaposed fields under steady conditions. This was simply arranged by viewing the mixture photometer glasses through a good bi-prism, size of field and brightness of retinal image being made the same as for the flicker photometer work. The procedure in obtaining the brightness discrimination fraction was to use one light only, for which the green was taken, and turn the two opal glasses relative to each other until a difference of brightness was just noticeable between the two halves of the bi-prism, when the angle

* Equation (11) can be used to calculate the critical speeds for all hue differences lying between any two for which ω_M has been determined, by noting that halving the colour difference between the compared fields is equivalent to doubling the value of δ_H , &c. Critical speed hue difference curves when calculated in this way have the general characteristics of the experimental one just published by Troland ("Apparent Brightness," Illuminating Engineering Society Convention, 1916). The critical speed for elimination of colour flicker between equally bright fields is a measure of their hue difference which may prove easier to determine than the present method of stepping off just noticeable differences. It should be possible to connect these critical speeds with the colour triangle.

† δ_H could also be obtained directly by a similar method to that used for δ_B by finding the critical speeds for various intermediate hue differences.

was read. Readings were made in both directions of rotation, and half the difference taken as the least perceptible rotation, which was then translated into brightness discrimination fraction with the aid of the data of fig. 4. The hue discrimination fraction was obtained in an exactly similar manner, both lights being used in this case, and the glasses being rotated until a difference of hue appeared between the two halves of the bi-prism.

These two steady observation discrimination fractions will be denoted as Δ_B and Δ_H . Whether these fractions or the mean error of setting most nearly compare with the δ 's need not be discussed here, for we shall merely use the ratio of the two, which will be practically the same whichever measure of perception difference is taken.

The complete investigation of the various discrimination fractions and their relationship consists of five sets of measurements, which should be performed at one sitting in view of the apparent variability of some of them. These five measurements are as follows:—

1. Determination of δ_B .
2. Determination of equal brightness condition for two colours to be used for hue discrimination test.
3. Determination of δ_H by critical speed measurements of two colours separately and together.
4. Determination of Δ_B .
5. Determination of Δ_H .

Three complete sets as thus outlined were carried through: two by the writer and a third by Mr. Kingsbury. The results are tabulated below:—

| | $\log \delta_B$ | $\log \delta_H$ | $\frac{\delta_H}{\delta_B}$ | Δ_B | Δ_H | $\frac{\Delta_H}{\Delta_B}$ | $\frac{\delta_H}{\delta_B} \cdot \frac{\Delta_H}{\Delta_B}$ |
|---------------|-----------------|-----------------|-----------------------------|------------|------------|-----------------------------|---|
| H. E. I. | -3.7 | -2.79 | 8.1 | .034 | .034 | 1.0 | 8.1 |
| " " " | -4.2 | -3.09 | 13.0 | .025 | .03 | 1.2 | 10.8 |
| E. F. K. | -3.2 | -2.07 | 13.5 | .044 | .08 | 1.8 | 7.4 |
| Mean | | | | | | | 8.8 |

The last column shows in a very striking manner to what the flicker photometer owes its peculiar applicability to colour difference work. *In the confusion condition caused by rapid alternation the appreciation of hue difference fails to*

keep pace with the appreciation of brightness difference. How necessary this eight- to ten-fold difference in the relative hue and brightness discriminations for steady and flicker conditions is, is shown graphically in fig. 7, where the upper dashed colour flicker curve (calculated by the aid of equation (11)), is the one which would condition the sensibility if the two discrimination fractions maintained the same relative values they have for steady juxtaposed fields. There would be no sensibility at all. This was further verified by attempting to operate the mixture photometer with the two glasses turned to the point of just noticeable hue difference. Either light source could then be placed practically anywhere on the photometer track without altering the brightness match.

This breakdown of hue discrimination is, of course, only another way of stating the common "explanation" of the flicker photometer, that "colour flicker ceases before brightness flicker." This is, however, the first time that definite measurements have been made of the visual constants whose values result in this condition. The explanation now needed is one step further back, namely, why does hue difference discrimination fail in the ultimate receiving apparatus with rapidly alternating impressions?

It may be suggested, as a start toward an explanation, that colour discrimination is probably a later development than brightness discrimination, and that under conditions of confusion or stress the more primitive function maintains its characteristics with less impairment. The supposition may be hazarded that in general with the senses appreciation of quality differences is much easier disturbed than that of intensity differences. A close parallel to the action of the visual apparatus, as revealed by these measurements, is furnished by a flow-meter, such as a gas-meter, to which is attached an apparatus for indicating the kind of gas going through, the latter being conceived as a more complicated device requiring some time to respond. As long as only one kind of gas flows through the measurement of rate and the indication of composition are equally satisfactory. But let two different gases flow through in rapidly varying proportions. The precision of the gas-meter will be unchanged, but the composition indicator will be quite unable to respond to each momentary condition.

9. *Effect of Choice of Speed on Flicker Photometer Settings.*

In the first theoretical paper the condition which must be satisfied when a setting is made on the flicker photometer was studied and found to be expressible by the equation

$$2I_1e^{-\frac{X_1}{\sqrt{2K_1}}\sqrt{\omega}} = 2I_2e^{-\frac{X_2}{\sqrt{2K_2}}\sqrt{\omega}}. \quad \dots (12)$$

The assumption was then made (assumption 3 of that paper), that the position of setting is independent of the speed, and the relationship of the flicker setting to the equal intensity and equal critical speed setting was developed for an assumed constant speed. In the light of the more recent work this assumption is no longer necessary, nor is it rigidly true. Inspection of fig. 7, for instance, shows that the bisector of the no-flicker region in the case of two different colours is inclined toward the colour of lower critical speed, so that the higher the working speed the more this will be favoured.

Introducing the complete expression for the diffusivity in terms of the critical speed-illumination relation, (12) becomes

$$\log I_1 - \frac{\sqrt{\omega} \log \frac{2}{\delta_B}}{\sqrt{a_1 \log I_1 + b_1}} = \log I_2 - \frac{\sqrt{\omega} \log \frac{2}{\delta_B}}{\sqrt{a_2 \log I_2 + b_2}}, \quad (13)$$

in which the values of I_1 and I_2 which satisfy the equation are the ones which will be adjudged equal by the flicker photometer criterion, when the alterations occur at the speed ω .

This expression shows that the point of setting is different for different speeds, and at the same time that *the approach to equal brightness setting is closer the lower the speed*. This emphasizes again the importance of avoiding all mechanical flicker and of selecting the speed for each colour difference.

Obviously ω should be the critical speed for the appearance of colour flicker, which has been called ω_M above. This is given in terms of δ_H and δ_B in equation (11), which transposed is,

$$\omega_M = \frac{\omega_R + \omega_G}{2} \left(\frac{\log \frac{2}{\delta_H}}{\log \frac{2}{\delta_B}} \right)^2 \dots \dots (14)$$

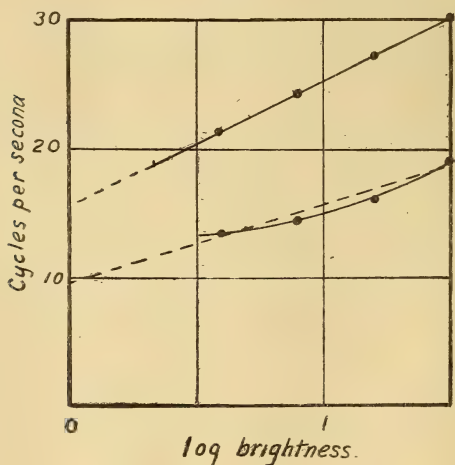
Substituting this in (13), the *complete expression* for the behaviour of the equal exposure flicker photometer, when

operated at the point of just-disappearance of colour flicker, is

$$\begin{aligned} \log I_1 - \log \frac{2}{\delta_H} \sqrt{\frac{(a_1 \log I_1 + b_1) + (a_2 \log I_2 + b_2)}{2(a_1 \log I_1 + b_1)}} \\ = \log I_2 - \log \frac{2}{\delta_H} \sqrt{\frac{(a_2 \log I_2 + b_2) + (a_1 \log I_1 + b_1)}{2(a_2 \log I_2 + b_2)}}. \end{aligned} \quad \dots (15)$$

In making this substitution for δ_H two assumptions figure : first, the one leading to equation (11), that the critical speed of the mixture of the two compared colours may be calculated to a close approximation by disregarding the different diffusivities of the two colours ; and second, that δ_H is constant over the range of intensities in question. If these assumptions are true, then equation (14) states (δ_B having been found constant over wide range, as shown by the data of fig. 6) that the plot of ω_M against $\log I$ should be a straight line, lying below the mean straight line given by the critical frequencies for the two compared colours, and inclined to it at such an angle that both intersect the axis of abscissæ at a common point.

Fig. 8.



Upper points, mean critical frequencies for red and green light. Lower points, critical frequencies for red and green alternated against each other.

This relationship was tested out experimentally with the result shown in fig. 8, where the upper, straight line is

the mean of the red and green light critical speed points, and the lower line is the critical speed plot for red and green alternated (the mean illumination being the same as for each alone) at their equality setting. The relationship between critical speed and log brightness shows a well-marked deviation from the rectilinearity which would result were both the above assumptions correct. This is not surprising, for hue difference discrimination for steady observation varies quite rapidly with brightness, and in the flicker photometer the working speed at low intensities will be larger than that predicted from these assumptions owing to the pronounced lag of one colour impression behind another * and the consequent lack of exact dove-tailing.

In spite of the failure of relation (14) to hold exactly, it gives the order of magnitude of ω_M so closely that the result of using (15) with δ_H as a constant will be correct to within the probable errors of any experimental test. When used for calculations similar to those made in the first paper with ω assumed constant, the resultant predicted behaviour of the flicker photometer is quite similar, the deviations from the equal brightness position of setting being of course smaller, but decreasing with increased intensity as before. It may, in fact, be questioned whether the calculations made on the constant speed assumption do not more nearly represent the experimental conditions holding when the data with which they were compared were obtained, since some mechanical flicker undoubtedly prevented the use of as low speeds as the colour differences used would warrant. It is to be hoped that data of this sort collected in future will be made with the polarization flicker photometer.

It may be noted, in passing, that the use of a variable instead of a constant speed in the calculation of the behaviour of the flicker photometer helps in the discussion of the unequal exposure instrument treated in the second paper. For by reducing the value of the constant F in equation (14) of that paper the relative intensities necessary for a setting of the instrument are brought nearer together, in agreement with the experimental data.

10. Summary.

The results of this investigation may be summarized as follows :—

1. A polarization flicker photometer has been constructed, in which the transition from one field to the other is gradual

* See "Visual Diffusivity," Ives, Phil. Mag. Jan. 1917.

and follows exactly the cosine curve assumed in the previous theoretical discussion of the flicker photometer.

2. By the use of this photometer it has been possible to verify in exact quantitative manner the relationships between relative intensity and absolute intensity of compared fields and critical speeds, as previously calculated from theory.

3. Measurements have been made of the brightness and hue discrimination fractions for both steady and fluctuating impressions.

4. It has been found that the applicability of the flicker photometer to colour difference comparisons is due to the failure of hue discrimination as compared with brightness discrimination under conditions of rapid fluctuation, and the amount of this failure has been determined by measurement.

5. A complete expression has been worked out for the behaviour of the flicker photometer in terms of the critical frequency-illumination relations for the two compared colours, and the hue discrimination fraction for fluctuating impressions.

I am greatly indebted to Mr. E. R. Morton for assistance in the construction of the experimental apparatus and in making the readings, and also to Mr. Kingsbury and Dr. Karrer for the series of observations made by them.

Physical Laboratory,
The United Gas Improvement Company,
Philadelphia, Pa.
September 13th, 1916.

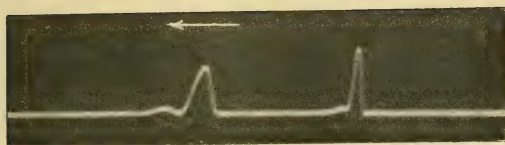
XXXVII. *Notices respecting New Books.*

Annuaire pour l'an 1917 publié par le Bureau des Longitudes.
Paris : Gauthier-Villars. Price 2 fr. net.

WITH very little delay appears this useful annual publication as though the world were at peace. Besides the usual astronomical tables there appear in this issue chapters on Metrology and Meteorology, besides special articles on (A) the Babylonian calendar, (B) summer-time 1916 by J. Renaud, (C) determination of the metre in terms of wave-lengths of light, by M. Hamy.

The article on summer-time, in particular, is of great historic interest in the summary it gives of the debates which took place in France and elsewhere prior to making this salutary change.

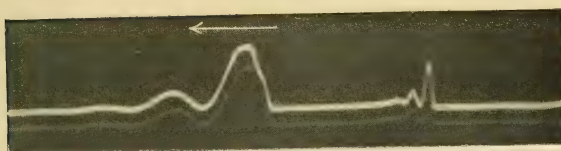
FIG. 1.



Break. Make.

Primary layers in series-parallel.

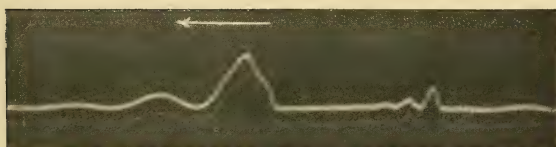
FIG. 2.



Break. Make.

Primary layers in series.

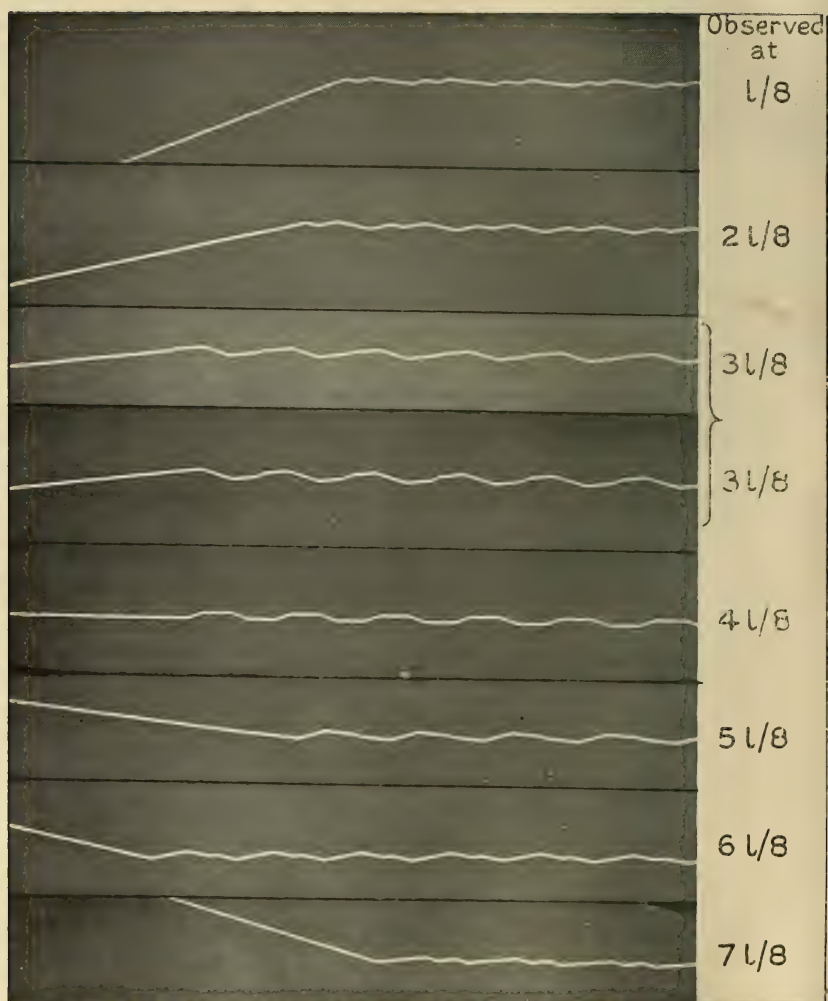
FIG. 3.



Break. Make.

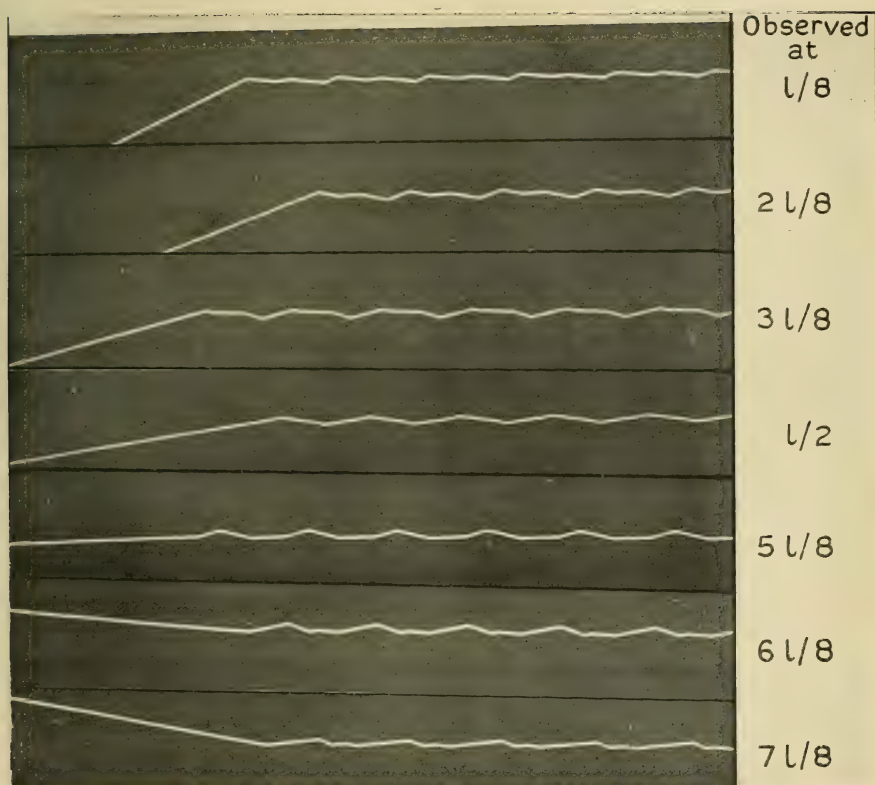
Layers in series, and series inductance.

FIG. 1.



Photographs of vibration-curves showing initial motion and subsequent vibration with two equal discontinuous changes of velocity.

FIG. 2.

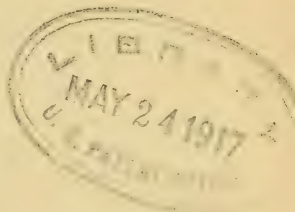


As in Fig. 1, but with two *unequal* discontinuous changes of velocity.

THE
LONDON, EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

[SIXTH SERIES.]

MAY 1917.



XXXVIII. *On Periodic Irrotational Waves at the Surface of Deep Water.* By Lord RAYLEIGH, O.M., F.R.S.*

THE treatment of this question by Stokes, using series proceeding by ascending powers of the height of the waves, is well known. In a paper with the above title† it has been criticised rather severely by Burnside, who concludes that “these successive approximations can not be used for purposes of numerical calculation...”. Further, Burnside considers that a numerical discrepancy which he encountered may be regarded as suggesting the non-existence of permanent irrotational waves. It so happens that on this point I myself expressed scepticism in an early paper‡, but afterwards I accepted the existence of such waves on the later arguments of Stokes, McCowan§, and of Korteweg and De Vries||. In 1911¶ I showed that the method of the early paper could be extended so as to obtain all the later results of Stokes.

The discrepancy that weighed with Burnside lies in the fact that the value of β (see equation (1) below) found best to satisfy the conditions in the case of $\alpha = \frac{1}{4}$ differs by about

* Communicated by the Author.

† Proc. Lond. Math. Soc. vol. xv. p. 26 (1915).

‡ Phil. Mag. vol. i. p. 257 (1876); ‘Scientific Papers,’ vol. i. p. 261.

§ Phil. Mag. vol. xxxii. pp. 45, 553 (1891).

|| Phil. Mag. vol. xxxix. p. 442 (1895).

¶ Phil. Mag. vol. xxi. p. 183 (1911).

50 per cent. from that given by Stokes' formula, viz. $\beta = -\frac{1}{2}\alpha^4$. It seems to me that too much was expected. A series proceeding by powers of $\frac{1}{4}$ need not be very convergent. One is reminded of a parallel instance in the lunar theory where the motion of the moon's apse, calculated from the first approximation, is doubled at the next step. Similarly here the next approximation largely increases the numerical value of β . When a smaller α is chosen ($\frac{1}{10}$), series developed on Stokes' plan give satisfactory results, even though they may not converge so rapidly as might be wished.

The question of the convergency of these series is distinct from that of the existence of permanent waves. Of course a strict mathematical proof of their existence is a desideratum; but I think that the reader who follows the results of the calculations here put forward is likely to be convinced that permanent waves of moderate height do exist. If this is so, and if Stokes' series are convergent in the mathematical sense for such heights, it appears very unlikely that the case will be altered until the wave attains the greatest admissible elevation, when, as Stokes showed, the crest comes to an edge at an angle of 120° .

It may be remarked that most of the authorities mentioned above express belief in the existence of permanent waves, even though the water be not deep, provided of course that the bottom be flat. A further question may be raised as to whether it is necessary that gravity be constant at different levels. In the paper first cited I showed that, under a gravity inversely as the cube of the distance from the bottom, *very long* waves are permanent. It may be that under a wide range of laws of gravity permanent waves exist.

Following the method of my paper of 1911, we suppose for brevity that the wave-length is 2π , the velocity of propagation unity*, and we take as the expression for the stream-function of the waves, reduced to rest,

$$\psi = y - \alpha e^{-y} \cos x - \beta e^{-2y} \cos 2x - \gamma e^{-3y} \cos 3x \\ - \delta e^{-4y} \cos 4x - \epsilon e^{-5y} \cos 5x, \quad . \quad . \quad (1)$$

in which x is measured horizontally and y vertically downwards. This expression evidently satisfies the differential equation

* The extension to arbitrary wave-lengths and velocities may be effected at any time by attention to dimensions.

to which ψ is subject, whatever may be the values of the constants α, β , &c. And, much as before, we shall find that the surface condition can be satisfied to the order of α^7 inclusive; $\beta, \gamma, \delta, \epsilon$ being respectively of orders $\alpha^4, \alpha^5, \alpha^6, \alpha^7$.

We suppose that the free surface is the stream-line $\psi=0$, and the constancy of pressure there imposed requires the constancy of U^2-2gy , where U , representing the resultant velocity, is equal to $\sqrt{\{(d\psi/dx)^2+(d\psi/dy)^2\}}$, and g is the constant acceleration of gravity now to be determined. Thus when $\psi=0$,

$$\begin{aligned} U^2-2gy &= 1+2(1-g)y+\alpha^2 e^{-2y}+2\beta e^{-2y} \cos 2x \\ &+4\gamma e^{-3y} \cos 3x+6\delta e^{-4y} \cos 4x+8\epsilon e^{-5y} \cos 5x \\ &+4\alpha\beta e^{-3y} \cos x+6\alpha\gamma e^{-4y} \cos 2x+8\alpha\delta e^{-5y} \cos 3x \quad . \quad (2) \end{aligned}$$

correct to α^7 inclusive. On the right of (2) we have to expand the exponentials and substitute for the various powers of y expressions in terms of x .

It may be well to reproduce the process as formerly given, omitting δ and ϵ , and carrying (2) only to the order α^5 . We have from (1) as successive approximations to y :—

$$y = \alpha e^{-y} \cos x = \alpha \cos x; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$y = \alpha(1-y) \cos x = -\frac{1}{2}\alpha^2 + \alpha \cos x - \frac{1}{2}\alpha^2 \cos 2x; \quad . \quad (4)$$

$$\begin{aligned} y &= \alpha(1-y+\frac{1}{2}y^2) \cos x \\ &= -\frac{\alpha^2}{2} + \alpha \left(1 + \frac{9}{8}\alpha^2\right) \cos x - \frac{\alpha^2}{2} \cos 2x + \frac{3\alpha^3}{8} \cos 3x, \quad (5) \end{aligned}$$

which is correct to α^3 inclusive, β being of order α^4 . In calculating (2) to the approximation now intended we omit the term in $\alpha\gamma$. In association with $\alpha\beta$ and γ we take $e^{-3y}=1$; in association with β , $e^{-2y}=1-2y$; while

$$\alpha^2 e^{-2y} = \alpha^2(1-2y+2y^2-\frac{4}{3}y^3).$$

Thus on substitution for y^2 and y^3 from (5)

$$\alpha^2 e^{-2y} = \alpha^2 \{1-2y+\alpha^2-4\alpha^3 \cos x + \alpha^2 \cos 2x - \frac{4}{3}\alpha^3 \cos 3x\}.$$

In like manner

$$2\beta e^{-2y} \cos 2x = 2\beta \cos 2x - 2\alpha\beta(\cos x + \cos 3x).$$

Since the terms in $\cos x$ are of the fifth order, we may replace $\alpha \cos x$ by y , and we get

$$\begin{aligned} U^2-2gy &= 1+\alpha^2+\alpha^4+2y(1-g-\alpha^2-2\alpha^4+\beta) \\ &+ (\alpha^4+2\beta) \cos 2x + (-\frac{4}{3}\alpha^5+4\gamma-2\alpha\beta) \cos 3x. \quad . \quad (6) \end{aligned}$$

The constancy of (6) requires the annullment of the coefficients of y and of $\cos 2x$ and $\cos 3x$, so that

$$\beta = -\frac{1}{2}\alpha^4, \quad \gamma = \frac{1}{12}\alpha^5, \quad . \quad . \quad . \quad (7)$$

and

$$g = 1 - \alpha^2 - \frac{5}{2}\alpha^4. \quad . \quad . \quad . \quad . \quad . \quad (8)$$

The value of g in (8) differs from that expressed in equation (11) of my former paper. The cause is to be found in the difference of suppositions with respect to ψ . Here we have taken $\psi = 0$ at the free surface, which leads to a constant term in the expression for y , as seen in (5), while formerly the constant term was made to disappear by a different choice of ψ .

There is no essential difficulty in carrying the approximation to y two stages further than is attained in (5). If δ , ϵ are of the 6th and 7th order, they do not appear. The longest part of the work is the expression of e^{-y} as a function of x . We get

$$e^{-y} = 1 + \frac{3\alpha^2}{4} + \frac{125\alpha^4}{64} - \cos x \{ \alpha + 2\alpha^3 \} \\ + \cos 2x \left\{ \frac{3\alpha^2}{4} + \frac{125\alpha^4}{48} - \beta \right\} - \frac{2\alpha^3}{3} \cos 3x + \frac{125\alpha^4}{192} \cos 4x, \quad (9)$$

and thence from (1)

$$y = -\frac{1}{2}\alpha^2 - \alpha^4 + \cos x \left\{ \alpha + \frac{9\alpha^3}{8} + \frac{625\alpha^5}{192} - \frac{3\alpha\beta}{2} \right\} \\ - \cos 2x \left\{ \frac{1}{2}\alpha^2 + \frac{4\alpha^4}{3} - \beta \right\} + \cos 3x \left\{ \frac{3\alpha^3}{8} + \frac{625\alpha^5}{384} - \frac{3\alpha\beta}{2} + \gamma \right\} \\ - \frac{\alpha^4}{3} \cos 4x + \frac{125\alpha^5}{384} \cos 5x. \quad . \quad . \quad . \quad . \quad . \quad (10)$$

When we introduce the values of β and γ , already determined in (7) with sufficient approximation, we have

$$y = -\frac{1}{2}\alpha^2 - \alpha^4 + \cos x \left\{ \alpha + \frac{9\alpha^3}{8} + \frac{769\alpha^5}{192} \right\} \\ - \cos 2x \left\{ \frac{\alpha^2}{2} + \frac{11\alpha^4}{6} \right\} + \cos 3x \left\{ \frac{3\alpha^3}{8} + \frac{315\alpha^5}{128} \right\} \\ - \frac{\alpha^4}{3} \cos 4x + \frac{125\alpha^5}{384} \cos 5x, \quad . \quad . \quad . \quad . \quad . \quad (11)$$

in agreement with equations (13), (18) of my former paper when allowance is made for the different suppositions with respect to ψ , as may be effected by expressing both results in terms of a , the coefficient of $\cos x$, instead of α .

The next step is the further development of the pressure equation (2), so as to include terms of the order α^7 . Where β , γ , &c. occur as factors, the expression for y to the third order, as in (5), suffices; but a more accurate value is required in $\alpha^2 e^{-2y}$. Expanding the exponentials and replacing products of cosines by cosines of sums and differences, we find in the first place

$$\begin{aligned} U^2 - 2gy = & 2(1 - g - \alpha^2)y + 1 + \alpha^2 + \alpha^4 + \frac{19\alpha^6}{4} - 4\alpha^2\beta \\ & + \cos x \left\{ -4\alpha^5 + 2\alpha\beta - \frac{37\alpha^7}{2} + \frac{97\alpha^3\beta}{6} - \frac{9\alpha^2\gamma}{2} \right\} \\ & + \cos 2x \left\{ \alpha^4 + 2\beta + \frac{19\alpha^6}{3} - 2\alpha^2\beta \right\} \\ & + \cos 3x \left\{ -\frac{4\alpha^5}{3} - 2\alpha\beta + 4\gamma - \frac{37\alpha^7}{4} + \frac{13\alpha^3\beta}{4} + 3\alpha^2\gamma - 4\alpha\delta \right\} \\ & + \cos 4x \left\{ \frac{19\alpha^6}{12} + 2\alpha^2\beta - 6\alpha\gamma + 6\delta \right\} \\ & + \cos 5x \left\{ -\frac{37\alpha^7}{20} - \frac{25\alpha^3\beta}{12} + \frac{15\alpha^2\gamma}{2} - 12\alpha\delta + 8\epsilon \right\}. \quad (12) \end{aligned}$$

From the terms in $\cos x$ we now eliminate $\cos x$ by means of

$$\alpha \cos x = y \left(1 - \frac{9\alpha^2}{8} \right) + \frac{\alpha^2}{2} + \frac{\alpha^2}{2} \cos 2x,$$

thus altering those terms of (12) which are constant, and which contain y and $\cos 2x$. Thus modified, (12) becomes

$$\begin{aligned} U^2 - 2gy = & 1 + \alpha^2 + \alpha^4 + \frac{11\alpha^6}{4} - 3\alpha^2\beta \\ & + 2y \left\{ 1 - g - \alpha^2 - 2\alpha^4 + \beta - 7\alpha^6 + \frac{167\alpha^2\beta}{24} - \frac{9\alpha\gamma}{4} \right\} \\ & + \cos 2x \left\{ \alpha^4 + 2\beta + \frac{13\alpha^6}{3} - \alpha^2\beta \right\} \\ & + \cos 3x \left\{ -\frac{4\alpha^5}{3} - 2\alpha\beta + 4\gamma - \frac{37\alpha^7}{4} + \frac{13\alpha^3\beta}{4} + 3\alpha^2\gamma - 4\alpha\delta \right\} \\ & + \cos 4x \left\{ \frac{19\alpha^6}{12} + 2\alpha^2\beta - 6\alpha\gamma + 6\delta \right\} \\ & + \cos 5x \left\{ -\frac{37\alpha^7}{20} - \frac{25\alpha^3\beta}{12} + \frac{15\alpha^2\gamma}{2} - 12\alpha\delta + 8\epsilon \right\}. \quad (13) \end{aligned}$$

The constant part has no significance for our purpose, and the term in y can be made to vanish by a proper choice of g .

If we use only α , none of the cosines can be made to disappear, and the value of g is

$$g = 1 - \alpha^2 - 2\alpha^4 - 7\alpha^6. \quad (14)$$

When we include also β , we can annul the term in $\cos 2x$ by making

$$\beta = -\frac{\alpha^4}{2} \left(1 + \frac{29\alpha^2}{6} \right), \quad (15)$$

and with this value of β

$$g = 1 - \alpha^2 - \frac{5\alpha^4}{2} - \frac{619\alpha^6}{48}. \quad (16)$$

But unless α is very small, regard to the term in $\cos 3x$ suggests a higher value of β as the more favourable on the whole.

With the further aid of γ we can annul the terms both in $\cos 2x$ and in $\cos 3x$. The value of β is as before. That of γ is given by

$$\gamma = \frac{\alpha^5}{12} \left(1 + \frac{139\alpha^2}{8} \right), \quad (17)$$

and with this is associated

$$g = 1 - \alpha^2 - \frac{5\alpha^4}{2} - \frac{157\alpha^6}{12}. \quad (18)$$

The inclusion of δ and ϵ does not alter the value of g in this order of approximation, but it allows us to annul the terms in $\cos 4x$ and $\cos 5x$. The appropriate values are

$$\delta = -\frac{\alpha^6}{72}, \quad \epsilon = \frac{\alpha^7}{480}, \quad (19)$$

and the accompanying value of γ is given by

$$\gamma = \frac{\alpha^5}{12} \left(1 + \frac{413\alpha^2}{24} \right), \quad (20)$$

while β remains as in (15).

We now proceed to consider how far these approximations are successful, for which purpose we must choose a value for α . Prof. Burnside took $\alpha = \frac{1}{4}$. With this value the second term of β in (15) is nearly one-third of the first (Stokes') term, and the second term of γ in (20) is actually larger than the first. If the series are to be depended upon, we must clearly take a smaller value. I have chosen $\alpha = \frac{1}{10}$, and this makes by (15), (18), (20)

$$\beta = -0.000,052,42, \quad \gamma = 0.000,000,976, \quad g = 0.989,736,92. \quad (21)$$

The next step is the calculation of approximate values of y from (11), which now takes the form

$$y = -\cdot0051 + \cdot101,165,0 \cos x \\ - \cdot005,183,3 \cos 2x + \cdot000,399,6 \cos 3x \\ - \cdot000,033,3 \cos 4x + \cdot000,003,3 \cos 5x. \dots (22)$$

For example, when $x=0$, $y=\cdot091,251,3$. The values of y calculated from (22) at steps of $22\frac{1}{2}^\circ$ (as in Burnside's work) are shown in column 2 of Table I.

We have next to examine how nearly the value of y afforded by (22) really makes ψ vanish, and if necessary to calculate corrections. To this δ and ϵ in (1) do not contribute sensibly and we find $\psi = +\cdot000,015,4$ for $x=0$. In order to reduce ψ to zero, we must correct the value of y . With sufficient approximation we have in general

$$\delta\psi = \delta y (1 + \frac{1}{10} e^{-y} \cos x)^*,$$

or in the present case

$$\delta y = -\frac{\cdot000,015,4}{1\cdot091} = -\cdot000,014,1,$$

so that the corrected value of y for $x=0$ is $\cdot091,237,2$. If we repeat the calculation, using the new value of y , we find $\psi=0$.

TABLE I.

| x . | y from (22). | y corrected. | $U^2 - 2gy - 1$. | Corrected by $\delta\beta$. |
|------------------|-------------------|-------------------|-------------------|------------------------------|
| 0 | $+\cdot091,251,3$ | $+\cdot091,237,2$ | $\cdot010,104,9$ | 45 |
| $22\frac{1}{2}$ | $+\cdot084,839,7$ | $+\cdot084,841,9$ | $\dots 4,7$ | 44 |
| 45 | $+\cdot066,182,8$ | $+\cdot066,181,8$ | $\dots 4,3$ | 43 |
| $67\frac{1}{2}$ | $+\cdot036,913,1$ | $+\cdot036,915,1$ | $\dots 4,1$ | 44 |
| 90 | $+\cdot000,050,0$ | $+\cdot000,052,4$ | $\dots 4,2$ | 46 |
| $112\frac{1}{2}$ | $-\cdot039,782,7$ | $-\cdot039,780,2$ | $\dots 4,4$ | 47 |
| 135 | $-\cdot076,316,2$ | $-\cdot076,317,5$ | $\dots 4,3$ | 43 |
| $157\frac{1}{2}$ | $-\cdot102,381,1$ | $-\cdot102,395,1$ | $\dots 4,7$ | 44 |
| 180 | $-\cdot111,884,7$ | $-\cdot111,907,9$ | $\cdot010,105,1$ | 47 |

In the fourth column are recorded the values of $U^2 - 2gy - 1$, calculated from (1) with omission of δ and ϵ , and with the corrected values of y . $d\psi/dx$, $d\psi/dy$ were first found separately, and then U^2 as the sum of the two squares. The values of β , γ , g employed are those given in (15), (18), (20). The form of ψ in (1) with these values of the constants vanishes when y takes the values of the third column, and the pressure

* The double use of δ will hardly cause confusion.

at the surface is also constant to a high degree of approximation. The greatest difference is $(\cdot000,001,0)$, which may be compared with $\cdot4$, the latter amount representing the corresponding statical difference at the crest and trough of the wave. According to this standard the pressure at the surface is constant to $2\frac{1}{2}$ parts in a million.

The advantage gained by the introduction of β and γ will be better estimated by comparison with a similar calculation where only α (still equal to $\frac{1}{16}$) and g are retained. By (2) in this case

$$U^2 - 2gy - 1 = \alpha^2 e^{-2y} + 2(1-g)y. \quad (23)$$

Table II. shows the values of y and of $\alpha^2 e^{-2y}$ corresponding to the same values of x as before. The fourth column gives (23) when g is so determined as to make the values equal at 0° and 180° . It appears that the discrepancy in the values of $U^2 - 2gy$ is reduced 200 times by the introduction of β and γ , even when we tie ourselves to the values of β , γ , g prescribed by approximations on the lines of Stokes.

TABLE II.

| $x.$ | $y.$ | $\alpha^2 e^{-2y}.$ | $U^2 - 2gy - 1.$ |
|------------------|--------------|---------------------|------------------|
| 0 | +·091,276,5 | ·008,331,4 | ·010,207,7 |
| $22\frac{1}{2}$ | ·084,870,5 | ·008,438,8 | ... 183,4 |
| 45 | ·066,182,4 | ·008,760,2 | ... 120,7 |
| $67\frac{1}{2}$ | ·036,882,6 | ·009,288,9 | ... 047,1 |
| 90 | 0 | ·010,000,0 | ... 000,0 |
| $112\frac{1}{2}$ | --·039,823,1 | ·010,829,0 | ... 010,4 |
| 135 | --·076,318,5 | ·011,649,0 | ... 080,2 |
| $157\frac{1}{2}$ | --·102,344,1 | ·012,271,4 | ... 167,6 |
| 180 | --·111,832,6 | ·012,506,5 | ·010,207,7 |

A cursory inspection of the numbers in column 4 of Table I. suffices to show that an improvement can be effected by a slight alteration in the value of β . For small corrections of this kind it is convenient to use a formula which may be derived from (2). We suppose that while α and ψ are maintained constant, small alterations $\delta\beta$, $\delta\gamma$, δg are incurred. Neglecting the small variations of β , γ , g when multiplied by α^2 and higher powers of α , we get

$$\begin{aligned} \delta y = & \delta\beta \{ \cos 2x - \frac{3}{2}\alpha \cos x - \frac{3}{2}\alpha \cos 3x \} \\ & + \delta\gamma \{ \cos 3x - 2\alpha \cos 2x - 2\alpha \cos 4x \}, \quad (24) \end{aligned}$$

and

$$\begin{aligned} \delta(U^2 - 2gy) = & 2\alpha(\delta\beta - \delta g) \cos x + 2\delta\beta \cos 2x \\ & + 2(2\delta\gamma - \alpha\delta\beta) \cos 3x - 6\alpha\delta\gamma \cos 4x. \quad (25) \end{aligned}$$

For the present purpose we need only to introduce $\delta\beta$, and with sufficient accuracy we may take

$$\delta(U^2 - 2gy) = 2\delta\beta \cos 2x. \quad . \quad . \quad . \quad (26)$$

We suppose $\delta\beta = -\cdot000,000,2$, so that the new value of β is $-\cdot000,052,6$. Introducing corrections according to (26) and writing only the last two figures, we obtain column 5 of Table I., in which the greatest discrepancy is reduced from 10 to 4—almost as far as the arithmetic allows—and becomes but one-millionth of the statical difference between crest and trough. This is the degree of accuracy attained when we take simply

$$\psi = y - \alpha e^{-y} \cos x - \beta e^{-2y} \cos 2x - \gamma e^{-3y} \cos 3x, \quad . \quad (27)$$

with $\alpha = \frac{1}{10}$, g and γ determined by Stokes' method, and β determined so as to give the best agreement.

XXXIX. *The Application of Solid Hypergeometrical Series to Frequency Distributions in Space.* By S. D. WICKSELL, Dr. Phil., Lund, Sweden*.

IN the number of this Journal issued in September 1914, Dr. L. Isserlis, under the above title, published a paper on the fitting of hypergeometrical series to correlation surfaces. The problem to describe curves of variation by aid of hypergeometrical series was treated as long ago as 1895 by Prof. Pearson in his classical Memoir: "Skew Variation in Homogeneous Material," Phil. Trans. vol. clxxxvi. Later, in 1899, Prof. Pearson gave a fuller discussion of the hypergeometrical series (Phil. Mag. vol. xlvii.). It is this paper that is the starting-point and chief place of reference of Dr. Isserlis. On the whole, the hypergeometrical series and its special case for $n = \infty$, the binomial series, play a dominating part in Prof. Pearson's celebrated theory of variation of one variate. As a consequence hereof, it was natural that the attempt should be made to employ solid hypergeometrical series as a means to describe also surfaces of correlation. Hereby, however, a fact has evidently been overlooked that greatly limits the range of applicability of any hypergeometrical or multinomial types of correlation functions. Of course, there must be some identical relations between the moments that should be more or less fulfilled in all cases of application. Dr. Isserlis also produces several such relations. But it is evident that he has not ascribed too much importance to these limitations. In the theory of variation of one variate there are similar conditions, but they

* Communicated by the Author.

have proved to be of only little harm to the generality of the frequency-curves generated. Now, the writer of these lines has reason to think that the limitations in case of the application to correlation surfaces is of far greater importance. The fact which is the ground for the opinion of the writer is the following: *All surfaces of correlation described by aid of the multinomial or hypergeometrical series must necessarily have linear regression.* With regard to the multinomial correlation function, which is the coefficient of $x^s y^{s'}$ in the development of $(p_1 xy + p_2 x + p_3 y + p_4)^r$, the fact has already been demonstrated in my paper in *Svenska Aktuari-föreningens Tidskrift*, Nr. 4-5, 1916 (see also *Meddelanden från Lunds Astronomiska Observatorium*, 1916).

In order to prove our proposition also in case of the solid hypergeometrical series, we must first recall the formulation of the corresponding chance problem. In Dr. Isserlis' own words it is: a bag contains n balls of which np are white and nq are black; r balls are drawn and not replaced; a second draw of r' balls is made. This is repeated N times. If N is a large number, the theoretical frequency of s black balls in the first draw and s' in the second is (in a somewhat different notation)

$$\frac{N \cdot r! r'! (qn)! (pn)! (n-r-r')!}{s! s'! (r-s)! (r'-s')! (qn-s-s')! (pn-r-r'+s+s')! n!}$$

Calling this function $z(s, s')$, the moments p'_{ij} may be deduced either, as does Dr. Isserlis, with the aid of a system of differential equations or more directly by performing the summations

$$p'_{ij} = \sum_{s, s'} z(s, s') s^i s'^j,$$

by which method recursion formulæ for the moments are easily derived. Especially it will readily be found that the mean values of s and s' are

$$p'_{10} = rq; \quad p'_{01} = r'q.$$

Thus it is seen that the means of the number of "lucky" events are equal to the product of the number of trials and the probability of a "lucky" event at the *beginning of the drawings*. Now, it is an easy task to show that the regression is linear. Indeed, if from the N sets of drawings we pick out all that have given a certain number, say $s=S$ black balls in the first r trials, they will all have that in common, that the second set of r' drawings has been extracted from a bag that contained $n-r$ balls, of which only $qn-S$ were black. Hence, for these samples, if N be a large enough

number, the mean of the number of black balls in the second sets of trials will be

$$s'_s = \frac{r'(nq - S)}{n - r} \dots \dots \dots (1)$$

Thus the mean value of s' for a given value of s is a linear function of s , by which the linearity of regression is proved.

It will be of some interest to see how the moments of the hypergeometrical series, as found by Dr. Isserlis, are consistent with the general conditions for linear regression, and especially how these conditions are even contained in the identical relations between the moments as far as such have been deduced. First, we must, however, find the relations between the moments that are the necessary conditions of linearity of regression. Denoting by ξ and η the deviations from the means $s - rq$ and $s' - r'q$, we must (as from the above regression formula it is obvious that when $S = rq$ we have $s'_s = r'q$) give to the equation of the regression line of, for instance, s' on s , the form

$$\eta_\xi = b\xi \dots \dots \dots (2)$$

Denoting the coefficient of correlation by ρ and the standard deviations of s and s' by σ and σ' , we necessarily have

$$b = \rho \cdot \frac{\sigma'}{\sigma} \dots \dots \dots (3)$$

The truth of formula (3) is well known and may be demonstrated in the following way. Multiplying (2) with

$$\xi \sum_{\eta} z(\xi + rq, \eta + r'q)$$

and summing for all values of the variable ξ , we obtain

$$\sum_{\xi} \xi \eta_{\xi} \sum_{\eta} z(\xi + rq, \eta + r'q) = b \sum_{\xi} \xi^2 \sum_{\eta} z(\xi + rq, \eta + r'q) \dots (4)$$

According to the signification of η_{ξ} as a mean of η for constant ξ , this may be written

$$\sum_{\xi} \sum_{\eta} \xi \eta z(\xi + rq, \eta + r'q) = b \sum_{\xi} \sum_{\eta} \xi^2 z(\xi + rq, \eta + r'q)$$

or, denoting by p_{ij} the moments about the mean of $z(s, s')$,

$$p_{11} = bp_{20}.$$

As $\rho = \frac{p_{11}}{\sqrt{p_{20}p_{02}}}$, we have thus proved the truth of (3).

The equation of the regression line is hence

$$\eta_{\xi} = \rho \frac{\sigma'}{\sigma} \xi \dots \dots \dots (5)$$

In order to derive the general relations between the moments that are a consequence of the linearity of regression we proceed thus: Multiplying (5) by

$$\xi^2 \sum_{\eta} z(\xi + r q, \eta + r' q),$$

we find, summing for all values of ξ ,

$$p_{21} = \rho \frac{\sigma'}{\sigma} p_{30} \quad \text{or} \quad p_{21} p_{20} = p_{30} p_{11} \cdot \cdot \cdot \cdot \cdot \quad (6)$$

This formula has been deduced by Pearson in his well-known memoir on the skew regression.

Multiplying further by

$$\xi^3 \sum_{\eta} z(\xi + r q, \eta + r' q)$$

and summing, we obtain

$$p_{31} p_{20} = p_{10} p_{11}, \cdot \cdot \cdot \cdot \cdot \cdot \cdot \quad (7)$$

and similarly proceeding for higher powers of ξ and having recourse also to the equation of the other regression line, we have as conditions of linear regression,

$$\begin{aligned} p_{a,1} p_{20} &= p_{a+1,0} p_{11}, \\ p_{1,\beta} p_{12} &= p_{0,\beta+1} p_{11} \cdot \cdot \cdot \cdot \cdot \cdot \cdot \quad (8) \end{aligned}$$

Dr. Isserlis has not deduced the moments p_{31} and p_{13} , so we are not in a position to test his formulæ on linearity of regression otherwise than in case of the moments of the third order. In case of these moments Dr. Isserlis has found the identical relations

$$\begin{aligned} p_{21} p_{20} p_{03} &\equiv p_{12} p_{02} p_{30}, \\ p_{02} p_{20} p_{21} p_{12} &\equiv p_{11}^2 p_{03} p_{30}. \end{aligned}$$

Dividing these relations, we find

$$\begin{aligned} p_{21}^2 p_{20}^2 &= p_{30}^2 p_{11}^2, \\ p_{12}^2 p_{02}^2 &= p_{03}^2 p_{11}^2. \end{aligned}$$

Taking regard of the fact that according to the results of Dr. Isserlis, the moments p_{20} and p_{11} as well as the moments p_{30} and p_{21} have inverse signs, we see that the identities contain in them the conditions of linear regression

$$\begin{aligned} p_{21} p_{20} &= p_{30} p_{11}, \\ p_{12} p_{02} &= p_{03} p_{11}. \end{aligned}$$

Obviously, as the regression has already been shown to be strictly linear, it should be found on deducing the moments of higher order than the third that the hypergeometrical series is subject to the general identities

$$p_{\alpha, 1} p_{20} = p_{\alpha+1, 0} p_{11},$$

$$p_{1, \beta} p_{02} = p_{0, \beta+1} p_{11}.$$

Of course, these are not the only relations possible to find, also relations between the pure marginal moments are at hand.

The application of solid hypergeometrical series to correlation surfaces must, as we have shown, be confined to cases of strictly linear regression. That this has not been observed by Isserlis is evident, as otherwise he would have mentioned it, or, at least, he would not have attempted to apply the series to a case of decidedly curvilinear regression, as in the example of the correlation of the ages of bachelors and spinsters at the epoch of marriage. As regards the example of the numbers of trumps in whist, the regression is linear, but there is an error in the computation of the correlation coefficient, which is -0.3305 , not -0.2559 .

Note I.—The chance problem that gives rise to the above-mentioned multinomial series is the following: A bag contains n balls. The balls are either white or black, besides being marked by either an even or an odd number. Of the balls np_1 are black and even, np_2 are black and odd, np_3 are white and even, and np_4 are white and odd; r balls are drawn and each ball is replaced after drawing. This is repeated N times. If N is a large number, the theoretical frequency of sets with s black balls and s' even balls is the coefficient of $x^s y^{s'}$ in the development of

$$(p_1 xy + p_2 x + p_3 y + p_4)^r.$$

The moments of this series are deduced in my memoir in the *Meddelanden från Lunds Astronomiska Observatorium* cited above. The regression is strictly linear. If the balls are not replaced there arises a series in which the terms are certain sums of the terms of a hypergeometrical series in three dimensions. Hereby the regression will still be strictly linear, as the even balls in samples of $s=S$ black balls come forth as if they had been drawn in S trials from a bag containing all the black balls and in $r-S$ trials from a bag containing all the white balls of the initial bag. The mean of the number of even balls in samples of S black balls will

then be the sum of two quantities, of which the one is proportional to S and the other to $r-S$, thus being a linear function of S .

Note II.—We have shown above that the condition for linear regression is that the following relations between the moments are valid :

$$p_{\alpha, 1} p_{20} = p_{\alpha+1, 0} p_{11},$$

$$p_{1, \beta} p_{02} = p_{0, \beta+1} p_{11}.$$

Introducing the notations

$$\Sigma_{ij} = \frac{p_{ij}}{\sigma^i \sigma^{ij}},$$

we may write the conditions thus

$$\alpha! \rho_{\alpha+1, 0} = \Sigma_{\alpha, 1} - \rho \Sigma_{\alpha+1, 0} = 0,$$

$$\beta! \rho_{0, \beta+1} = \Sigma_{1, \beta} - \rho \Sigma_{0, \beta+1} = 0.$$

When the regression is not linear the quantities $\rho_{i, 0}$ and $\rho_{0, j}$, or some of them, will not disappear. In another place I shall soon demonstrate that the equations to the curves of regression, when the correlation is only moderately skew, may be expressed in a very convenient form with the aid of the coefficients $\rho_{i, 0}$ and $\rho_{0, j}$.

By Pearson's definition there is no correlation when the regression is linear and parallel to the axes. Though this definition seems to me to be not quite sufficient, as it does not necessarily coincide with the definition required from the standpoint of the theory of probability, *i. e.* that the variates should be separated in the correlation function, it is any way the best one to have recourse to when we have no adequate correlation function available. In the sense of Pearson's definition the variates will be independent of each other if all the coefficients ρ , ρ_{30} , ρ_{03} , ρ_{40} , ρ_{04} , &c. are zero. ρ is the usual coefficient of correlation; as the quantities ρ_{30} , ρ_{03} , ρ_{40} , ρ_{04} , &c., are abstract numbers, independent of any units, I propose that they be called the coefficients of correlation of higher order. The numerical factors are inserted for purposes of which I hope soon to give the explanation.

XI. Results of Crystal Analysis.—IV.

By L. VEGARD, Dr. phil., University of Christiania *.

[Plate IX.]

PART I.—The Structure of Ammonium Iodide and Tetramethylammonium Iodide.

§ 1. **T**HE substances NH_4I and $\text{N}(\text{CH}_3)_4\text{I}$ are the first members of a series which show very interesting morphotropic relations, and have attracted much attention from crystallographers†.

The crystals of NH_4I belong to the cubic system. When the four hydrogen atoms, however, are replaced by four alkyl groups (four CH_3 groups, say) the crystal becomes tetragonal, with the ratio c/a decreasing with increasing number of C atoms.

It would be natural to suppose the tetragonal structure to be produced by some tetragonal arrangement of the carbon atoms; and an attempt to explain the morphotropic relation between NH_4I and $\text{N}(\text{CH}_3)_4\text{I}$ has been made by P. Groth ‡.

According to his assumption, the NH_4I crystals should have the following structure:—The I atoms should be arranged in a simple cubic lattice, which is centred with a similar lattice of the N atoms. The hydrogen atoms should be placed on the cube-diagonals through the N atoms, in such a way that the H atoms are placed in the corners of a tetrahedron with the N atoms at the centre.

The structure of $\text{N}(\text{CH}_3)_4\text{I}$ he simply derives from that of its parent substance, by supposing the H atoms replaced by the group CH_3 in such a way that the C atoms take up a similar position to that previously occupied by the H atoms, and the H atoms of the CH_3 group are supposed to be placed in the corner of a tetrahedron with the C atom at its centre.

Although these hypothetical lattices of Groth show several striking points of similarity with those actually found, it will be seen that the morphotropic relation between the two substances is not quite so simple as that supposed by Groth.

The topic parameters, as calculated by Groth, for the

* Communicated by the Author.

† P. Groth, *Chemische Crystallographie*.

‡ See Stefan Kreutz, *Element der Theorie der Krystallstruktur*, p. 145 (1915).

four successive members of these substances are given in Table I.

TABLE I.

| | $v.$ | $\chi.$ | $\psi.$ | $\omega.$ | Symmetry. |
|--|--------|---------|---------|-----------|-------------|
| NH_4I | 57.51 | 3.860 | 3.860 | 3.860 | Cubic. |
| $\text{N}(\text{CH}_3)_4\text{I}$ | 108.70 | 5.319 | 5.319 | 3.842 | Tetragonal. |
| $\text{N}(\text{C}_2\text{H}_5)_4\text{I}$ | 162.91 | 6.648 | 6.648 | 3.686 | „ |
| $\text{N}(\text{C}_3\text{H}_7)_4\text{I}$ | 235.95 | 6.093 | 7.851 | 4.933 | „ |

Analysis of NH_4I .

§ 2. The crystals which were used for the Röntgen-ray analysis had the form of small cubes with faces (100), and were obtained by gradual evaporation of an aqueous solution of ammonium iodide.

The reflexion from the (100) face was easily obtained, and that of the face (110) was got from an edge formed by two (100) faces. To get the spectrum from (111), we had to grind an artificial surface as nearly as possible parallel to the (111) face.

The glancing angles and the relative intensities of spectra of different orders are given in Table II., and graphically in fig. 1.

TABLE II.

| Face. | Glancing angle. Order ... | Intensities. | | | |
|-------|------------------------------|--------------|----|----|----|
| | | 1. | 2. | 3. | 4. |
| (100) | 4° 50' | 100 | 33 | 11 | |
| (110) | 6 51 | 100 | 31 | 11 | |
| (111) | 4 08 | 100 | 90 | 20 | 20 |

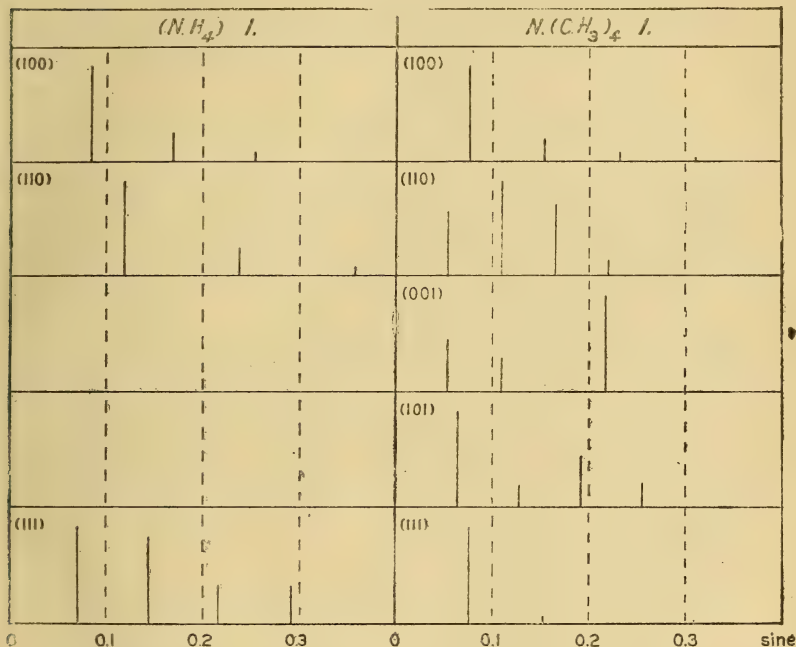
The spacing $d_{100} = 3.60 \times 10^{-8}$ cm. In the elementary cell there is $1/2$ molecule.

We are then naturally led to assume that the atoms are arranged in face-centred cubic lattices. The spacings of the other two faces are also in agreement with this assumption, for we find from the observed glancing angle:

$$\sin \theta_{100} : \sin \theta_{110} : \sin \theta_{111} = 1 : \sqrt{2} : 1/2\sqrt{3}. \quad . \quad . \quad (1)$$

From the intensity measurements we easily find that the face-centred lattice of N can be made to cover the lattice by a displacement $a/2$ parallel to one of the cube sides. Thus the N and I lattices are in the same relative opposition as the Na and Cl lattices in rock-salt.

Fig. 1.



If we do not take into account the small reflecting-power of hydrogen, this arrangement mentioned would give a normal distribution of intensities for the faces (100) and (110) in agreement with observations.

In the (111) face the N atoms are situated in planes midway between the I planes, which will produce a diminution of the intensity of the first and third order spectrum, which is also clearly brought out by the experiments.

With regard to the H atoms, their reflecting-power is probably too small to enable any experimental determination of their exact position. Most probably the four atoms which belong to each molecule are placed in the corners of a tetrahedron with the N atom in the centre, and in such a way that the lines from the N atom to any of the four H atoms are parallel to one of the diagonals of the cubic lattice.

The tetrahedron itself has a hemihedral form ; but this does not mean that the structure of the whole lattice is hemihedral. The structure will be holohedral provided the following conditions are fulfilled:—

- (1) The tetrahedra must form two groups. The tetrahedra of each group may be brought to coincidence with one another by a translation only, and a tetrahedron of one group may be made to cover one of the other one by a translation and a rotation of 90° about an axis parallel to one of the sides of the cube.
- (2) The centres of the tetrahedra of any one of the groups must be arranged with holohedral symmetry.

We easily see that these conditions cannot be fulfilled if we suppose hydrogen to have an elementary lattice of the same size as those of I and N. For in that case all the tetrahedra belonging to the same elementary lattice of N atoms must be parallel. Now the whole structure only contains four elementary lattices of N atoms, and one of the groups of tetrahedra should have their centres in two elementary lattices ; but two elementary lattices forming part of a face-centred lattice cannot be arranged with cubic symmetry, and thus the second condition cannot be fulfilled. If, then, hydrogen has elementary lattices of the same size as those of I and N, all tetrahedra must be parallel and the symmetry of the lattice will be hemihedral (hexakistetrahedral) of the class 31.

A holohedral symmetry we could get if the side of the elementary lattice of H was twice that of N and I. Then the tetrahedra belonging to each single elementary lattice of nitrogen could be arranged in two different positions in such a way that the conditions (1) and (2) were fulfilled.

Thus our considerations have led to the result that the structure must either be holohedral or possess the symmetry of the hexakistetrahedral class. The latter arrangement, which would make the elementary lattice of H equal to that of N, is very simple and should seem the more probable.

With regard to the symmetry of the crystal, it is supposed to be hemihedral ; but the kind of hemihedrism is not quite certain. Groth put it down as pentagonikositetrahedral. Which of the two possible arrangements of the hydrogen atoms is the one which is able to explain the symmetry of crystal, further investigation must decide. There is, however, very little hope that the Röntgen-ray analysis can give us the exact position of the H atoms.

We must be aware that the symmetry properties of the crystal need not be expressed in the geometry of the lattice. The symmetry of the crystal may also depend on the symmetry properties of the centres. We know already several instances of this kind. Thus the holohedral lattices of KBr, KI, and Cu_2O give crystals of the pentagonikositetrahedric class.

A stereoscopic reproduction of a model corresponding to the hexakistetrahedral arrangement is given in Pl. IX. (a).

Analysis of $\text{N}(\text{CH}_3)_4\text{I}$.

§ 3. The crystals were got by gradual evaporation of an aqueous solution of $\text{N}(\text{CH}_3)_4\text{I}$. The crystals obtained were, however, quite small (greatest linear extension about 5-6 mm.), and had only the faces (111) and (100) developed. The reflexions for the other faces were got from edges—a circumstance which may to a certain extent reduce the accuracy of the intensity measurements for those faces.

Table III. and fig. 1 give the observed glancing angles and relative intensities for each face.

TABLE III.

| Face. | θ . | Intensities. | | | |
|-------|---------------|--------------|-----|-------|-----|
| | | $n=1$. | 2. | 3. | 4. |
| (100) | $4^\circ 25'$ | 100 | 24 | 11 | 4 |
| (110) | 3 09 | 68 | 100 | 76 | 18 |
| (001) | 3 07 | 55 | 35 | 0 (?) | 100 |
| (101) | 3 41 | 100 | 24 | 53 | 26 |
| (111) | 4 23 | 100 | 7.8 | 2 (?) | 5 |

From the observed glancing angles we find

$$= 3.94 \times 10^{-8} \text{ cm.}$$

and

$$d_{110} : d_{001} : d_{101} : d_{111} : d_{100} = 1.40 : 1.42 : 1.199 : 1.008 : 1,$$

or, approximately,

$$= \sqrt{2} : 2 \frac{c}{a} : \frac{2}{\sqrt{1 + \left(\frac{a}{c}\right)^2}} : \frac{2}{\sqrt{2 + \left(\frac{a}{c}\right)^2}} : 1.$$

The number of molecules in the elementary cell $d_{100}^2 d_{001}$ is found to be $1/2$.

First of all, we shall notice the form of the elementary cell. For the first time during our investigations on the tetragonal crystals, we meet with the case that the ratio d_{001}/d_{100} is not equal to the ratio of the axes c/a , but equal to twice this ratio.

This is a point of great value when we are going to determine the arrangement of the atoms.

Determination of the Lattice.

§ 4. The determination of the lattice was, indeed, more difficult than at first expected. It will at once be apparent from a comparison with the lattice found for NH_4I that we do not derive the lattice of $\text{N}(\text{CH}_3)_4\text{I}$ by a simple substitution with CH_3 . This is evident from the different ratios of the spacings d_{100} and d_{110} for the two crystals.

The first question to decide is, What is the size and form of our elementary lattice? At first it might seem possible that the elementary lattice had the same form as the elementary cell. Let the side of the base of the elementary lattice be a' and its height c' ; then we might have $c'/a' = \frac{2c}{a}$.

This assumption, however, did not lead to any possible arrangement, and is also very unlikely from a crystallographic point of view: thus a (111) plane of the lattice would correspond to a (221) plane of the crystal.

To avoid such difficulties, we must put

$$\frac{c'}{a'} = \frac{c}{a} \dots \dots \dots (3)$$

Now in the volume of the elementary lattice, which has at least one atom at each corner, there must be at least one molecule.

If we make the simplest possible assumption, we should have

$$\left. \begin{array}{l} a' = 2d_{100} \\ \text{and } c' = d_{001} \end{array} \right\} \dots \dots \dots (4)$$

The volume of the elementary lattice, being four times that of the elementary cell, must contain 2 molecules.

Let us first consider the relative position of the two lattices. Let us, in the usual way, take one corner of one of the lattices as origin of a rectilinear coordinate system with the axes parallel to the sides of the lattice.

The construction-points of the I lattices must be (000) and $(\frac{a'}{2}, \frac{a'}{2}, Z)$, where Z is a parameter to be determined.

The (xy) coordinates of the second point are found from the condition that $d_{100} = \frac{1}{2}a'$.

With regard to Z , two values might naturally suggest themselves :

$$Z = \frac{c}{2} \quad \text{and} \quad Z = 0.$$

The first value is excluded because it would give a wrong spacing of the (001) face, and the second value is not possible because it would lead to a wrong spacing of the (101) face.

We are then led to consider Z as a parameter to be determined.

In order to preserve the tetragonal symmetry, the N lattices must be placed in such a way that each of them may be made to cover one of the I lattices by a translation parallel to the c axis.

Consequently, the construction-points of the two N lattices will be

$$(0, 0, -Z_1') \quad \text{and} \quad \left(\frac{a}{2}, \frac{a}{2}, Z - Z_1''\right).$$

If the arrangement is to give a bipolar tetragonal axis, the following relation must hold :

$$Z_1' = -Z_1'' = l, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where l is a parameter ; and putting

$$Z + l = \frac{c}{2} - l_0$$

we get for the construction-points of the I and N lattices :

$$\left. \begin{array}{ll} \text{For the I lattice : } (000), & (a/2, a/2, c/2 - (l_0 + l)), \\ \text{,, N ,, } & (00 - l), (a/2, a/2, c/2 - l_0). \end{array} \right\} \quad (6)$$

The arrangement will be more easily understood when we introduce the conception of molecules.

To each of the two I lattices corresponds one N lattice, the position of which is found by a translation along the c axis a distance l . In this way the atoms are naturally divided up into pairs consisting of one I and one N atom.

The line of length l , connecting the two atoms, we might call the molecular axis.

Now four C atoms and twelve H atoms must be placed in tetragonal arrangement round this axis, and we get a kind of molecular element.

The axis of each molecular element is unipolar, or the molecule has no symmetry-plane perpendicular to the c axis.

If, then, the crystal as a whole is going to have a bipolar

axis, the two systems of molecules which correspond to the two component elementary lattices must have their axes turned in opposite directions. This statement is equivalent to the condition expressed in equation (5).

Now we might naturally introduce the middle point between the I and N atoms on the molecular axis as point of reference for the determination of the position of the molecular elements. Choosing one such point as the origin of our coordinate system, the construction-points of the two molecular systems would be

$$(000) \text{ and } (a/2, a/2, c/2 - l_0). \quad . \quad . \quad . \quad (7)$$

Thus the arrangement of the molecules involves the determination of the parameter l_0 .

To this parameter is added those necessary for the determination of the molecular element itself. As the molecular axes of the two groups of molecules have opposite directions, each group of molecules must give tetragonal symmetry; and as each group only forms one simple elementary lattice,

Fig. 2 a.

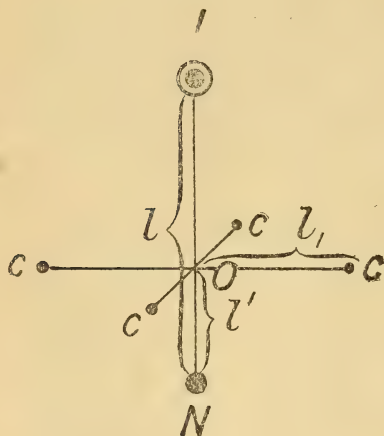


Fig. 2 b.



the C and H atoms must be arranged in such a way that each molecular element shows tetragonal symmetry with respect to the molecular axis. Further, in order to preserve the highest degree of tetragonal symmetry of the crystal, the planes through the axis and parallel to the sides of the lattice must be planes of symmetry. This condition considerably diminishes the possible arrangements of the atoms.

Fig. 2 a shows the most general arrangement of the C atoms round the tetragonal axis. In fig. 2 b the atoms

are projected on a plane perpendicular to the molecular axis. If we choose the position of one hydrogen atom, the symmetry conditions will give seven other positions where an H atom must be placed.

If we choose one position quite arbitrarily, we shall get eight atoms. If the number is to be reduced to four, we must place the H atom on one of the symmetry planes through the molecular axis either in position (1) or in position (2) (fig. 2 *b*).

From these considerations it follows that the most general arrangement of the atoms of a molecule involves the following parameters:—

- (1) The distance l between the I and the N atoms, or the length of the molecular axis.
- (2) The distance l_1 from a carbon atom to the molecular axis.
- (3) The distance l' from the N atom to the point where the plane of the C atoms intersects the molecular axis.
- (4) To arrange the twelve H atoms we may either divide them into three groups of four, or into one group of eight and one group of four as in fig. 2 *b*. The first possibility means that all H atoms are situated in the symmetry planes. As the determination of a point in a plane requires two parameters, this arrangement would involve six arbitrary parameters. The second possibility gives three parameters for the determination of the group of eight, and two parameters for the determination of the group of four.

A complete determination of the molecular element would require the knowledge of eight or nine parameters; and as one parameter is necessary to fix the position of the two groups of molecules, a complete knowledge of the structure of $\text{N}(\text{CH}_3)\text{I}$ should involve the determination of nine or ten parameters.

We shall see, however, that some of these parameters have very simple values, which will considerably simplify the lattice.

This type of lattice which we have sketched is a consequence of the assumption expressed in equation (4) and the symmetry properties of the crystal. If the equation (4) is right, the lattice must be able to explain the observed reflexion maxima. First of all, the lattice must give the

right spacings for the five faces. We easily find that the lattice gives the following spacings :—

$$d_{100} = \frac{1}{2} a', \quad d_{110} = \frac{a'}{2} \sqrt{2}, \quad d_{111} = \frac{a'}{\sqrt{2 + \left(\frac{a'}{c'}\right)^2}},$$

$$d_{101} = \frac{a'}{\sqrt{1 + \left(\frac{a'}{c'}\right)^2}}, \quad d_{001} = c'. \quad . \quad . \quad . \quad (8)$$

Comparing these values with the relations (2), we see that our lattice gives just the right spacing.

Determination of the Parameters.

§ 5. The general procedure for the determination of the parameters would be the following :—

We have first, for each face, to find the distribution of point planes within each period equal to the spacing of the face.

This distribution would be a function of the parameters. For a given distribution of planes we can calculate the distribution of intensities of various orders. Now we have observed relative intensities, or we know the *ratio* of the intensities of the spectra observed. We have observed four orders for each of the five faces, which should give fifteen ratios—corresponding to fifteen equations. These cannot all be independent. Thus, in our case, the intensities of the faces (100) and (110) only depend on four parameters, while they would give six equations. We are not going to carry out the calculation in this general way; but we shall adopt a procedure similar to the method of successive approximation.

We make use of the fact that the hydrogen atoms have a quite small reflecting power, and as the first approximation we can put the hydrogen atoms out of consideration. Then we have merely the four parameters l_0 , l , l' , and l_1 left for determination.

Now the problem is very much simplified by the fact that the intensities of the faces (100) and (110) do not depend on the parameters l_0 , l , l' , and we can determine l_1 separately.

First of all, we must remark that the molecular element may be placed in two different ways.

Either the lines OC (fig. 2a) can be parallel to the sides or to the diagonals of the base of the lattice. From the fact that the reflexion from the (100) face shows a nearly normal

distribution of intensities, while the first-order spectrum of (110) is very much reduced, we at once conclude that the latter possibility is excluded.

For the sake of convenience, we introduce the following new parameters :

$$\alpha = \frac{l_1}{a'} 2\pi, \quad \beta = \frac{l'}{c'} 2\pi, \quad \gamma = \frac{l}{c'} 2\pi, \quad \delta = \frac{l_0}{c'} 2\pi. \quad (9a)$$

Sometimes it will also be convenient to introduce

$$\alpha' = \pi - \alpha, \quad \gamma' = \pi - \gamma. \quad (9b)$$

Fig. 3.

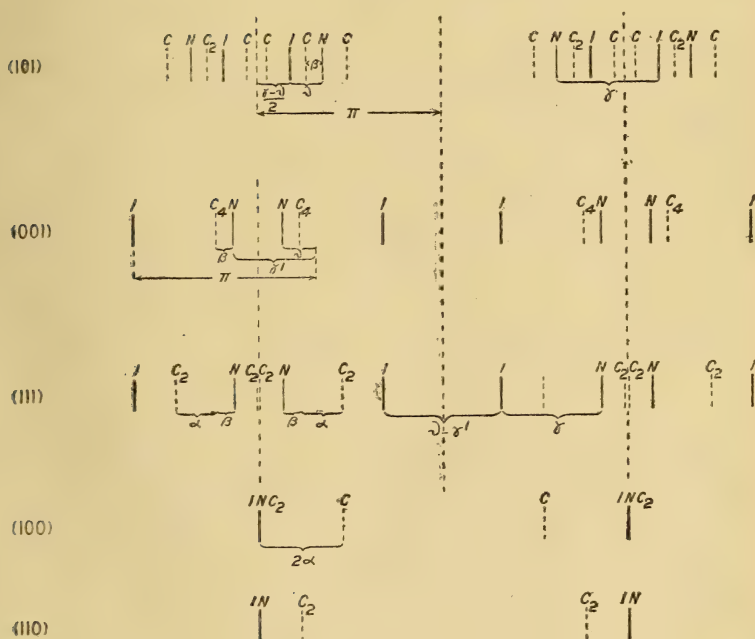


Fig. 3 gives the distribution of point planes for the five faces considered, and their position is given in terms of the angular parameters.

Let I, N, C, and H denote the atomic numbers ; then we get, after some reduction,

For the face (100),

$$A_n = I + N + 2C(1 + \cos 2n\alpha) ;$$

For the face (110),

$$A_n = I + N + 4C \cos n\alpha ;$$

For the face (001),

$$A_n = N \cos nA + 4C \cos nB + (-1)^n I \cos nC ;$$

For the face (101),

$$A_n = N \cos n\left(\frac{\pi}{2} - A\right) + 2C(\cos n\alpha + 1) \cos n\left(\frac{\pi}{2} - B\right) \\ + I \cos n\left(\frac{\pi}{2} - C\right) ;$$

For the face (111),

$$A_n = (-1)^n N \cos nA + 4C \cos n\alpha' \cos nB + I \cos nC ;$$

where

$$A = \frac{\gamma' - \delta}{2},$$

$$B = \frac{\gamma' - \delta}{2} + \beta,$$

$$C = \frac{\gamma' + \delta}{2}.$$

For the atomic numbers, we introduce

$$I = 53, \quad N = 7, \quad C = 6, \quad H = 1.$$

The fact that the atomic number of iodine is large as compared with those of the other atoms is of great value when we are going to determine the parameters.

From the faces (100) and (110), we find that the value of α must be near to 147° .

Let us, then, introduce the atomic numbers and divide by 7 ; then

$$\left. \begin{aligned} (001) \quad A_n &= \cos nA + 3.43 \cos nB + (-1)^n 7.57 \cos nC, \\ (111) \quad A_n &= (-1)^n \cos nA + 3.43 \cos n33^\circ \cos nB + 7.57 \cos nC, \\ (101) \quad A_n &= \cos n\left(\frac{\pi}{2} - A\right) + 1.72(1 + (-1)^n \cos n33^\circ) \cos n\left(\frac{\pi}{2} - B\right) \\ &\quad + 7.57 \cos\left(\frac{\pi}{2} - C\right), \end{aligned} \right\} \quad (12)$$

If we consider the expressions of A_n for the two faces (001) and (111), and compare them with the observed maxima of these faces, we can draw some very important conclusions.

The first point we notice is that the third-order spectrum of (111) almost vanishes. Now

$$\cos (3 \times 33) = -\cos 81$$

is a very small quantity ; and, as the last term of A_n will be dominating, we must have

$$\cos 3C \text{ nearly equal to } 0, \quad \text{or} \quad 3C = 90 \text{ or } 270.$$

The last possibility is excluded because it would make $\cos C$ a very small quantity, and we should not be able to explain the very strong first-order spectrum of this face.

Hence we conclude C near to 30° .

Now, also, the third-order spectrum of the (001) face is very small ; consequently, as $\cos 3C$ is small,

$$\cos 3B \text{ must be nearly equal to zero,}$$

$$\text{or} \quad 3B \text{ nearly equal to } 90^\circ \text{ or } 270^\circ.$$

The latter possibility is excluded because the first-order spectrum of (001) is to be quite small and $\cos B$ must have a fairly large positive value.

Thus we get

$$B \text{ nearly equal to } 30^\circ.$$

Thus we find

$$B \text{ nearly} = 30^\circ \text{ nearly} = C.$$

In order to find the best values of A , B , and C , we should have to give B and C values near to 30° and determine the amplitudes for the faces (111), (101), and (001) for various values of A .

If we carry out such a calculation, we find that we get the best possible agreement between calculated and observed values when we put

$$A = B = C = (\text{about}) 35^\circ. \quad . \quad . \quad . \quad (13)$$

The amplitudes calculated with this value of A , B , and C are given in Table IV., and also the values calculated from the observed intensities by means of the relation $I_n = k_n A_n^2$, where $k_1 = 1$, $k_2 = \frac{1}{3}$, $k_3 = \frac{1}{7}$, $k_4 = \frac{1}{12}$. We see that the agreement is quite satisfactory.

TABLE IV.

| | (001). | | (101). | | (111). | |
|----------------------|---------------|-----------|---------------|-----------|---------------|-----------|
| | From lattice. | From obs. | From lattice. | From obs. | From lattice. | From obs. |
| A ₁ | 28 | 21 | 50 | 52 | 100 | 100 |
| A ₂ | 45 | 30 | 36 | 44 | 44 | 48 |
| A ₃ | 9 | 0 | 100 | 100 | 19 | (?) |
| A ₄ | 100 | 100 | 69 | 72 | 62 | 72 |

Of course, we cannot prove that these three angles are exactly equal, but the difference cannot be more than a few degrees. Thus, if we put $B=30^\circ$ and $C=40^\circ$, or *vice versa*, we find intensities which are very different from those observed.

Inserting the values of A, B, and C from equation (11) equations (13) give

$$\left. \begin{aligned} A = B = C &= \frac{\gamma'}{2}, \\ \delta &= 0, \\ \beta &= 0. \end{aligned} \right\} \dots \dots \dots (14)$$

Thus we find that two of the parameters introduced are nearly equal to zero. From equation (9 a) we see that $l'=0$ and $l_0=0$.

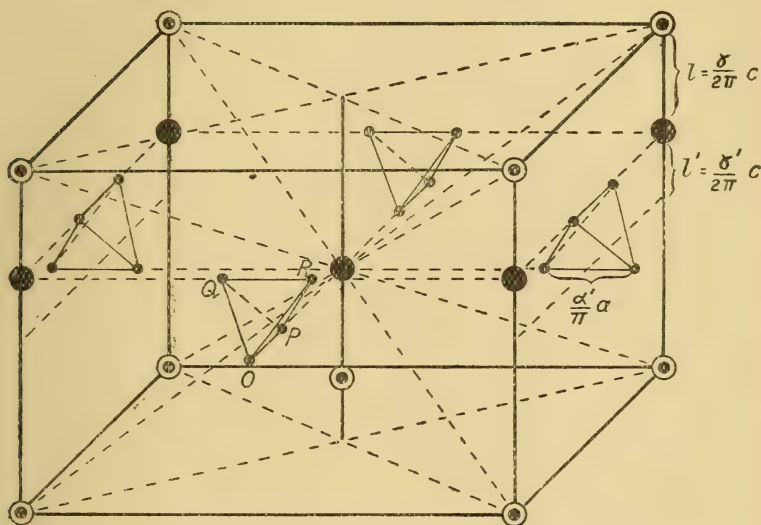
The disappearance of the first parameter l' means that in the molecular element the plane of the C atoms cuts the N atom, and $l_0=0$ means that the centres of the molecular axes are arranged in a "prism-centred" lattice. Or we might say that the N and I atoms are arranged in such a way that each elementary I lattice has an N lattice at its centre, and *vice versa*.

Thus the simple values found for l' and l_0 will considerably simplify the lattice.

The arrangement of the I, N, and C atoms is illustrated in fig. 4. We notice that the lattice found leads to a very simple arrangement of the C atoms. They appear in groups of four atoms belonging to four different molecular elements. These four C atoms are placed at the corners of a sphenoid (deformed tetrahedron) like OPQR. Two of the atoms of the group belong to the one elementary lattice of molecular

elements; the other two to the second molecular elementary lattice. The sphenoid, drawn on a larger scale, is represented in fig. 5, which also shows the dimensions expressed in terms of the two parameters α' and γ' and the sides a' and c' of the elementary lattice.

Fig. 4.



⊙ I atoms

● N "

• C "

The side $OP = \frac{\alpha'}{\pi} a'$, and the distance between the lines OP and QR is equal to $\frac{\gamma'}{2\pi} c'$.

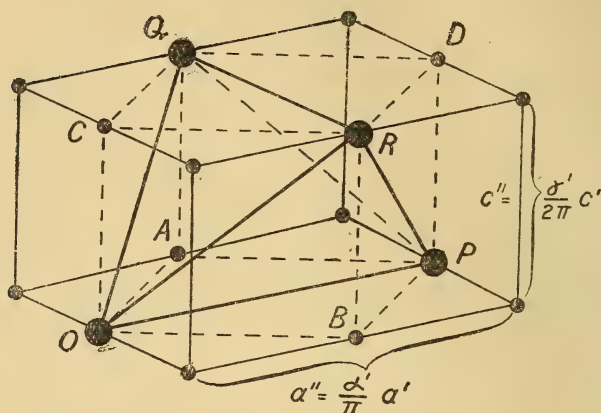
As shown in fig. 5, we can imagine the sphenoid placed inside a prism with a square base and with the carbon atoms placed at the middle points of four of the sides. The sides of the prism are parallel to corresponding sides of the lattice.

The side of the square base of the prism a'' is equal to OP or $\frac{\alpha'}{\pi} a'$; and the height c'' of the prism is equal to $\frac{\gamma'}{2\pi} c'$.

Consequently,

$$\frac{c''}{a''} = \frac{\gamma'/2}{\alpha'} \frac{c'}{a'}.$$

Fig. 5.



● C atoms

● H "

Thus, if we have

$$\frac{\gamma'}{2} = \alpha', \dots \dots \dots (15)$$

the small prism constructed on the C atoms should have exactly the same form as the elementary lattice. Now the approximate values found for the two parameters give $\frac{\gamma'}{2} = 35^\circ$ and $\alpha' = 33^\circ$, or the condition (15) is very nearly fulfilled. In fact, the difference between $\frac{\gamma'}{2}$ and α' is found to be so small that we may equally well satisfy the observation on the supposition that condition (15) is exactly fulfilled, so that we have

$$\frac{c''}{a''} = \frac{c'}{a'} = 0.722. \dots \dots \dots (16 a)$$

It might be of interest to find the ratio c''/a'' on the supposition that the C atoms were placed at the corners of a

real tetrahedron with all sides of equal length. Then we should have

$$\frac{c''}{a''} = \frac{1}{\sqrt{2}} = 0.707. \quad . \quad . \quad . \quad (16 b)$$

On account of the particular value of the ratio c/a , we get that, if condition (15) is fulfilled, the C atoms are placed at the corners of a sphenoid, which has very nearly the form of a tetrahedron.

The Arrangement of the Hydrogen Atoms.

§ 6. We saw that the positions of the hydrogen atoms were not necessarily fixed by symmetry; but when all requirements of symmetry were fulfilled, there would generally be at least five parameters left undetermined. As the reflecting power of the hydrogen atoms is very small as compared with that of the other atoms, a direct determination of the parameters would be very difficult, if at all possible.

On the other hand, the H atoms appear in such a great number that their reflecting power is by no means negligible; and if we have to choose between several *quite different* arrangements, the reflecting power of the H atoms may be great enough to enable us to make the right choice.

Now we have seen that the carbon atoms appear in groups of four, placed at the corners of a tetrahedron; and there is a comparatively small number of arrangements of the H atoms which should naturally present themselves. We shall consider the following three:—

(1) The three H atoms belonging to a certain C atom are placed on the three sides of the tetrahedron which pass through the C atom. This arrangement is shown in fig. 6. To fix the position of the H atoms on the lines, two parameters should be required, because the distance from the C atom O to the one H atom placed on the line OP parallel to the base plane may be different from the distance from the same atom to one of its two other H atoms. In view of the fact that all sides of the sphenoid are nearly equal, we should expect that also the three H atoms were placed at nearly equal distances from the C atom.

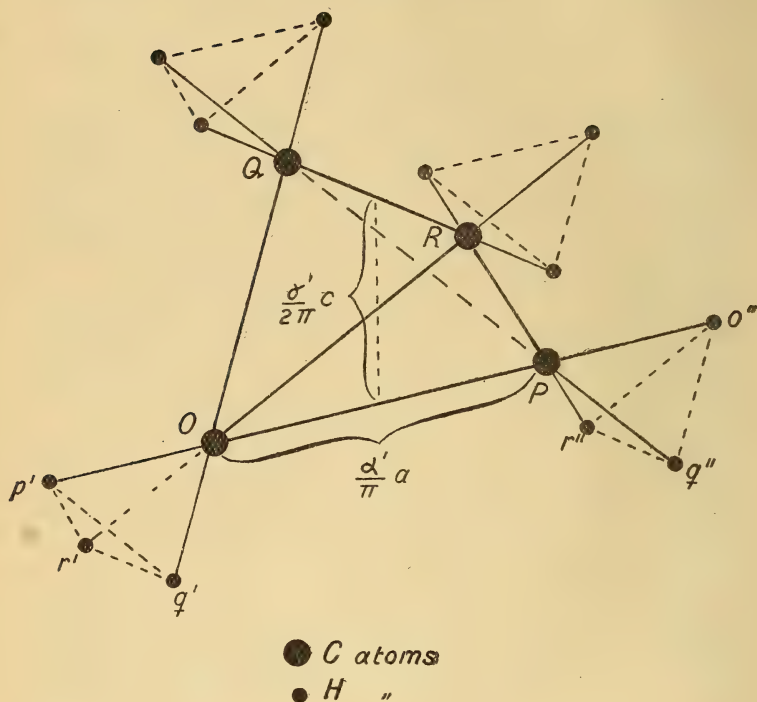
If the sides are not equal, the simplest assumption to make would be the following:—

One C atom and its three H atoms are placed at the corners of other sphenoids such as $O p' q' r'$, and we assume that these sphenoids are similar in form to the central one formed by the carbon atoms. In this way the positions

of the H atoms are determined by one parameter f , representing the ratio between corresponding sides of the sphenoids at the corners to those of the central one, *e. g.*,

$$f = \frac{Op'}{OP} = \frac{Or'}{OR} = \text{etc.} \quad (17)$$

Fig. 6.



(2) Another arrangement which would naturally suggest itself is shown in fig. 5. Eight of the twelve H atoms associated with the four C atoms are placed at the corners of the prism which can be constructed round the sphenoid $OPQR$, the other four H atoms are placed at those middle points of the sides of the base planes which are not occupied by the C atom. In this case the position of the H atoms would be determined without the introduction of any new parameter.

(3) We might also construct a prism round the sphenoid

in such a way that the C atoms were placed in two opposite corners of the base planes (O P A B Q R C D, fig. 5). It might also be natural to try to arrange the H atoms on the three sides of this prism which meet at the centre of a C atom. In this case, the positions of the H atoms are fixed by means of two parameters.

It can, however, be shown that the two latter arrangements do not give any satisfactory agreement with the observed intensities.

This can most easily be shown by means of the spectra from the faces (100) and (110).

Let us first consider the arrangement (2).

The amplitudes of the two faces (110) and (100) are given by the expressions :

$$(110) \quad A_n = 60 + 28 \cos n\alpha + (-1)^n 4 + 4 \cos n(2\alpha - \pi),$$

$$(100) \quad A_n = 74 + 22 \cos 2n(\pi - \alpha).$$

The intensity distribution of the (110) face might be explained by putting $\alpha = 140^\circ$. But this value of α would make the fourth-order spectrum of the face (100) much too strong. The amplitudes calculated from the lattice would be

$$100 \quad 68 \quad 80 \quad 117,$$

while those calculated from the observed intensities are

$$100 \quad 85 \quad 98 \quad 73.$$

The amplitudes of the face (001) would be given by the expression

$$A_n = (43 + (-1)^n 53) \cos n \frac{\gamma'}{2}.$$

In order to get the observed ratio for the spectra of first and second order, we should have to put $\frac{\gamma'}{2}$ equal to about 40° ; but then the fourth-order spectrum would be about ten times as strong as that of first order, while the ratio actually observed is merely 1:8.

As the amplitudes of (110) and (100) only depend on α , and those of (001) only on the parameter γ' , the test made is independent of the relation between the two parameters.

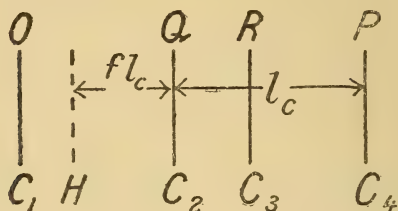
In the same way we can show, by a comparison with the faces (110), (100), and (001), that the arrangement (3) is unable to explain the observed distribution of intensities.

We are then to consider the arrangement (1) (fig. 6), which also, on account of the peculiar grouping of the C atoms, might seem the most probable.

The position of the hydrogen planes for any face is easily found from the assumption of similarity when we know the position of the C planes.

Let C_1, C_2, C_3, C_4 (fig. 7) be the positions of four C planes belonging to the same group of four atoms which are placed

Fig. 7.



at the corners of the spenoid, and passing through the four C atoms O, P, Q, R, respectively; then we easily see from fig. 6 how the three H planes belonging to any of the C atoms are going to be arranged. Let us, for example, find the H planes belonging to the C_2 planes. Let the distance between C and one of the other C planes be l_c ; then a corresponding H plane is found on the opposite side of C at a distance

$$l_H = fl_c,$$

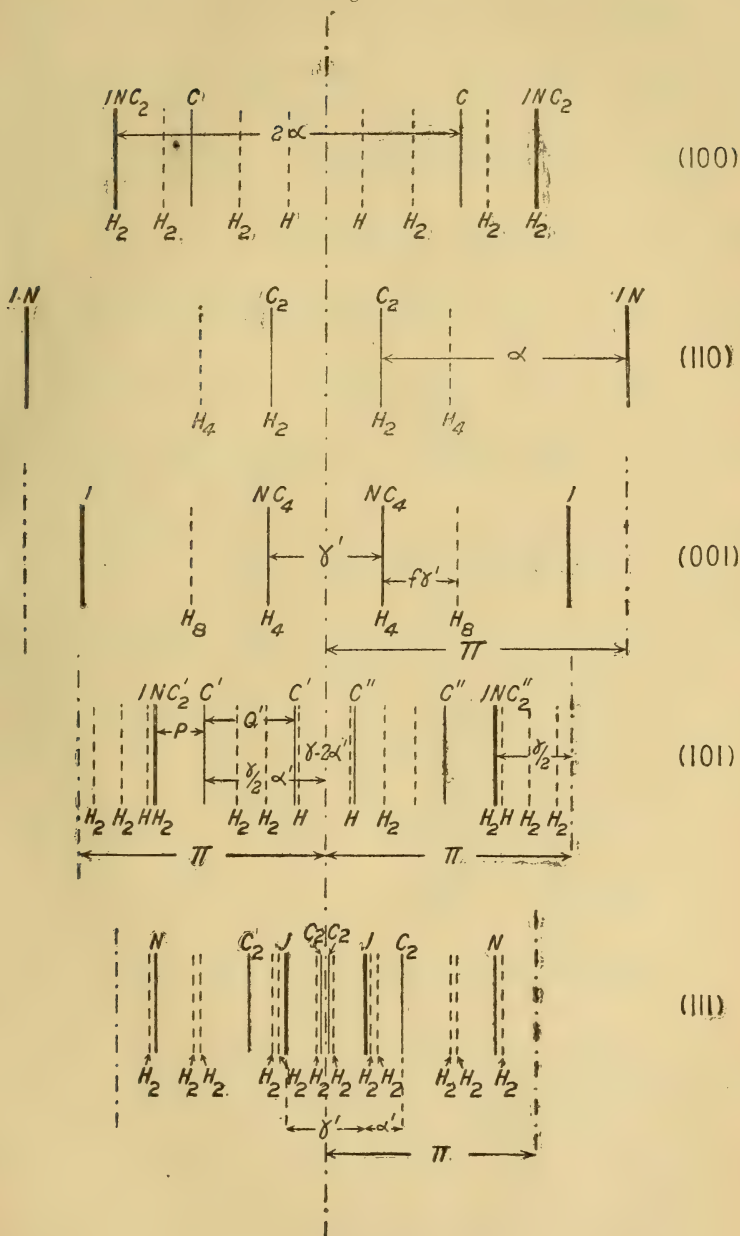
where f is the ratio given in equation (17).

The planes of the various atoms which form one period are represented in fig. 8 for the five faces in question. The arrangement of planes corresponds to the following values of the parameters

$$\gamma' = 70, \quad \alpha' = 33, \quad f = 0.64,$$

which are values which were found to give a satisfactory agreement between calculated and observed intensities.

Fig. 8.



In the way described we easily find the following expression for the amplitudes :

$$\begin{aligned}
 (100) \quad A_n &= I + N + 2C(1 + \cos 2n\alpha') + 2H[1 + 2 \cos 2nf\alpha' \\
 &\quad + 2 \cos 2n\alpha'(1+f) + \cos 2n\alpha'(1+2f)], \\
 (110) \quad A_n &= (I + N)(-1)^n + 4C \cos n\alpha' \\
 &\quad + 4H[\cos n\alpha' + 2 \cos n\alpha'(1+2f)], \\
 (001) \quad A_n &= (N + 4C + (-1)^n I) \cos n \frac{\gamma'}{2} \\
 &\quad + 4H \left[\cos n \frac{\gamma'}{2} + 2 \cos n \frac{\gamma'}{2} (1+2f) \right], \\
 (101) \quad A_n &= [(I + N + 2C)(-1)^n + 2C \cos n\alpha'] \cos n \left(\frac{\pi}{2} - \frac{\gamma'}{2} \right) \\
 &\quad + 2H(-1)^n \left[\cos n \frac{\gamma'}{2} + \cos n \left(\frac{\gamma'}{2} - f(\gamma' - \alpha') \right) \right. \\
 &\quad \left. + \cos n \left(\frac{\gamma'}{2} - f(\gamma' + \alpha') \right) \right] \quad (18 a) \\
 &\quad + 2H \left[\cos n \left(\frac{\gamma}{\alpha} + \alpha' - f(\gamma' - \alpha') \right) \right. \\
 &\quad \left. + \cos n \left(\frac{\gamma}{2} - \alpha' - f(\gamma' + \alpha') \right) \right] \\
 &\quad + H \left[\cos n \left(\frac{\gamma}{2} + \alpha' + 2f\alpha' \right) + \cos n \left(\frac{\gamma}{2} - \alpha' - 2f\alpha' \right) \right], \\
 (111) \quad A_n &= (I + (-1)^n N + 4C \cos n\alpha') \cos n \frac{\gamma'}{2} \\
 &\quad + 2H \left\{ \cos n \left[\left(\frac{\gamma'}{2} - \alpha' \right) (1+2f) \right] + \cos n \left(\frac{\gamma'}{2} - \alpha' + f\gamma' \right) \right. \\
 &\quad + \cos n \left(\frac{\gamma'}{2} - \alpha' - 2f\alpha' \right) + \cos n \left(\frac{\gamma'}{2} + \alpha' + 2f\alpha' \right) \\
 &\quad \left. + \cos \left(\frac{\gamma'}{2} + \alpha' + f\gamma' \right) + \cos n \left[\left(\frac{\gamma'}{2} + \alpha' \right) (1+2f) \right] \right\}.
 \end{aligned}$$

Also these formulæ, which take into account the effect of the hydrogen atoms, will give values of γ' and α' which very nearly satisfy the condition (15). The value of α' is most easily determined from the (110) face and that of γ' from the (001) face ; since for the first face the amplitudes only depend on α' and f , and for the second one only on γ' and f .

The amplitudes of these faces are also very sensitive to

differences in the position of the hydrogen atoms ; and from these faces we can determine the parameter f with an accuracy which is indeed greater than we might expect, on account of the small reflecting power of the hydrogen atoms.

If we would try to determine γ' and α' from the above formula, the best values would probably be

$$\alpha' = 34^\circ, \quad \frac{\gamma'}{2} = 35^\circ, \quad \text{and} \quad f = 0.5-0.6 ;$$

but we may, in fact, get an equally good agreement if we put

$$\frac{\gamma'}{2} = \alpha' = \phi,$$

and then the expression for the amplitudes takes the following simpler form :

$$(100) \quad A_n = 74 + 12 \cos n\phi + 2[2 \cos n 2f\phi + 2 \cos n 2(1+f)\phi + \cos n 2(1+2f)\phi]$$

$$(110) \quad A_n = 60(-1)^n + 28 \cos n\phi + 8 \cos n(1+2f)\phi,$$

$$(001) \quad A_n = (35 + (-1)^n 53) \cos n\phi + 8 \cos n(1+2f)\phi,$$

$$(101) \quad A_n = (72(-1)^n + 12 \cos n\phi) \cos n\left(\frac{\pi}{2} - \phi\right) \\ + 2(-1)^n \left[\cos n\left(\frac{\pi}{2} - \phi\right) + \cos n\left(\frac{\pi}{2} - (1+f)\phi\right) \right. \\ \left. + \cos n\left(\frac{\pi}{2} - (1+3f)\phi\right) \right] + 2 \cos n\left(\frac{\pi}{2} - f\phi\right) \\ + 2 \cos n\left(\frac{\pi}{2} - (2+3f)\phi\right) + \cos n\left(\frac{\pi}{2} + 2f\phi\right) \\ + \cos n\left(\frac{\pi}{2} - 2(1+f)\phi\right),$$

$$(111) \quad A_n = (53 + (-1)^n 7 + 24 \cos n\phi) \cos n\phi + 2 + 4 \cos 2nf\phi \\ + 4 \cos 2n(1+f)\phi + 2 \cos 2n(1+2f)\phi.$$

The value of ϕ can be found with a considerable accuracy. I have calculated the values of the amplitudes corresponding to various values of ϕ and f , and from the results of these

calculations I should give the following intervals for their values :

$$33 < \phi < 37,$$

$$+0.45 < f < 0.75 *.$$

In Table V. are given the amplitudes calculated from (18*b*) by putting

$$\phi = 35^\circ \quad \text{and} \quad f = 0.5;$$

and, for the sake of comparison, are given the amplitudes calculated directly from the observed intensities by means of the relation

$$A_n = \sqrt{\frac{I_n}{k_n}},$$

where we have put

$$k_1 = 1, \quad k_2 = 1/3, \quad k_3 = 1/7, \quad k_4 = 1/12.$$

TABLE V.

| Face. | Calculated from the lattice. | | | | Calculated from observations. | | | |
|-------|------------------------------|------------------|------------------|------------------|-------------------------------|------------------|------------------|------------------|
| | A ₁ . | A ₂ . | A ₃ . | A ₄ . | A ₁ . | A ₂ . | A ₃ . | A ₄ . |
| (100) | 100 | 90 | 85 | 73 | 100 | 85 | 98 | 73 |
| (110) | 46 | 86 | 100 | 54 | 36 | 75 | 100 | 63 |
| (001) | 18 | 36 | 3 | 100 | 21 | 30 | 0(?) | 100 |
| (101) | 51 | 33 | 100 | 68 | 52 | 44 | 100 | 72 |
| (111) | 100 | 42 | 13 | 58 | 100 | 48 | (weak) | 72 |

When we take into account the difficulty in obtaining accurate intensity values and the uncertainty with regard to k_n , the agreement between the values given by the lattice and those obtained from observation is very good. Although small differences may exist, the amplitudes calculated from the lattice will give just the typical distribution of intensities observed.

* It is to be remembered that we might also give f negative values, which would mean that the hydrogen atoms were placed on the lines *between* the C atoms of a group. But a negative value is unable to explain the intensity distribution.

The absolute dimensions of the lattice and the parameters will be

$$a' = 7.88 \times 10^{-8} \text{ cm.},$$

$$c' = 5.69 \times 10^{-8} \text{ cm.},$$

$$l_1 = \frac{\alpha}{2\pi} a' = 3.17 \times 10^{-8} \text{ cm.},$$

$$l = \frac{\gamma}{2\pi} c' = 1.76 \times 10^{-8} \text{ cm.}$$

The sides OP or QR of the tetrahedron (l_c):

$$l_c = \frac{\alpha'}{\pi} a' = 1.53 \times 10^{-8} \text{ cm.}$$

The distances Op' , Po'' , etc., from the C to the H atom:

$$Op' = f. l_c = 0.77 \times 10^{-8} \text{ cm.}$$

The distance between the carbon atom and one of its hydrogen atoms may probably be a little greater: perhaps the most probable value would be about 10^{-8} cm.

For the side of the cubic lattice of NH_4I , we found

$$7.20 \times 10^{-8} \text{ cm.}$$

Comparing this value with those found for a' and c' for $\text{N}(\text{CH}_3)_4\text{I}$, there is apparently no simple relation. One reason is obvious, and is simply this:

Inside a volume equal to the volume of the elementary lattice of $\text{N}(\text{CH}_3)_4\text{I}$ there are only two molecules, while the lattice of NH_4I contains four. *In spite of this fact, however, one molecule will on an average nearly take up the same space in the direction of the C axis.* We might find the sides of a prism similar in form to the elementary lattice, but only containing one molecule; then we should get

$$\text{For } \text{N}(\text{CH}_3)_4\text{I.} \begin{cases} \text{Side of the base} & . & . & 6.26 \times 10^{-8} \text{ cm.} \\ \text{Height of the prism} & . & . & 4.52 \times 10^{-8} \text{ cm.} \end{cases}$$

$$\text{For } \text{NH}_4\text{I.} \quad . \quad . \quad \text{Side of the cube} \quad . \quad . \quad 4.54 \times 10^{-8} \text{ cm.}$$

We see that the height of the prism in the first case is nearly equal to the side of the cube in the latter. This is, in fact, merely the well-known relation between the topic parameters, as shown in Table I. But it is, indeed, quite remarkable that a molecule takes up the same space in the

direction of the C axis, in spite of the fact that the *molecules* in the two cases are arranged in quite different lattices.

The analyses of these two substances have given the somewhat startling result that a simple relation between the topic parameters, such as that given in Table I., does not necessarily involve any very simple relation between the lattices.

In fact, the morphotropic relation might be most easily explained in the way proposed by Groth, by supposing that the I and N lattices were arranged in the same way in the two crystals. If the H atoms were substituted by C atoms and arranged tetragonally in planes perpendicular to the C axis, we should expect the lattice to expand in the direction perpendicular to the C axis, while in the direction of this axis the dimensions should be left unaltered.

Contrary to this supposition, the analysis has shown that the morphotropic relation is not explained by *substitution* alone; but the I and N lattices are not merely quite differently arranged, but the structure in the two cases contains a different *number* of elementary I and N lattices.

The NH_4I lattice is composed of 4 I, 4 N, and 12 H lattices; while the number of elementary lattices of $\text{N}(\text{CH}_3)_4\text{I}$ is

$$2 \text{ I, } 2 \text{ N, } 8 \text{ C, } 24 \text{ H.}$$

What determines the arrangement, we cannot at present tell; but generally there will be a tendency to form closely-packed systems, or that arrangement will be chosen which, under the conditions present, gives a minimum of potential energy due to the mutual attraction of the atoms.

Thus it is quite possible that a simple substitution (if such a lattice might be formed) would give a larger volume of the lattice and not give the observed simple relation between the topic parameters.

It was found that, in quite a formal way, we could imagine the $\text{N}(\text{CH}_3)_4\text{I}$ crystals composed of two molecular lattices; but in this case we must not put too much in the name—molecule. It may not be so that the affinity forces are mainly engaged to form the molecular element. Thus the groups of $(\text{CH}_3)_4$ which we have previously considered (fig. 6) may be kept together by forces of the same nature and order of size as those acting between the atoms of a single molecular element. This group, however, does not belong to a single molecular element, but is equally related to four different molecules.

The molecular element had four O atoms arranged tetragonally in a plane perpendicular to its axis, which, as in the previous cases of tetragonal crystals, give a natural explanation of the fact that the ratio c/a is smaller than unity.

Stereoscopic reproductions of a model of the lattice are shown in Pl. IX. (b) and (c).

PART II.—*Remarks concerning the Structure of Xenotime.*

§ 7. In the previous paper (III.*) I gave the results of an analysis of the crystal xenotime (YPO_4), and found a lattice which in the most satisfactory way would account for the spectra observed.

I mentioned that to get reflexion from this mineral was attended by considerable difficulties, on account of an internal transformation of the structure. Fairly good reflexions, which permitted a fairly accurate determination of the relative intensities, we only got from the faces (110) and (101). From the (100) face we only got the first- and second-order reflexion very weak; and from the (111) face we merely obtained one single maximum, which we took to be that of the fourth-order spectrum. For the (001) face we did not obtain any reflexion at all.

More recently I have greatly improved my experimental arrangements, partly by using a new Röntgen-ray bulb and partly by increasing the sensitiveness of the electrical arrangements for measuring the ionization current; and I undertook a new series of measurements of the reflexions from xenotime under these improved conditions.

The result was very satisfactory, and we succeeded in observing several weak maxima which we had not previously been able to detect. Thus we could measure the three first maxima of the (111) face and determine the spectrum from the base, which previously had given no detectable reflexion.

The spectra of the five faces (100), (110), (001), (101), and (111), as we finally found them, are given in Table VI. and in fig. 9.

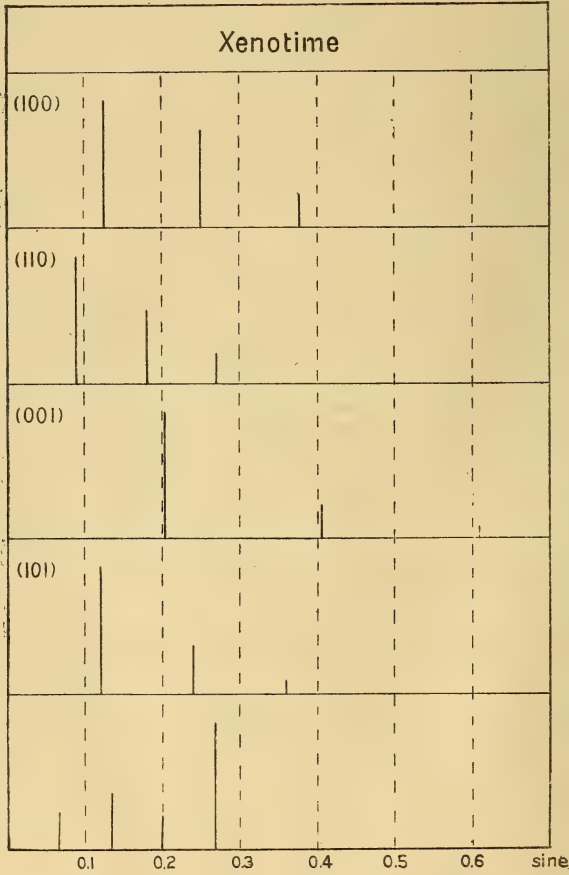
Comparing the spectra of xenotime with those of zircon, we notice that the analogy between them has now become much more marked.

* L. Vegard, *Phil. Mag.* xxxii. (1916) p. 505.

TABLE VI.

| Face. | | <i>n.</i> | | | |
|-------|--------|-----------|----|----|-----|
| | | 1. | 2. | 3. | 4. |
| (100) | 7° 16' | 100 | 77 | 23 | 100 |
| (110) | 5 9 | 100 | 58 | 25 | |
| (001) | 11 43 | 100 | 25 | 8 | |
| (101) | 6 58 | 100 | 40 | 13 | |
| (111) | 3 52 | 28 | 44 | 28 | |

Fig. 9.



The new measurements will not produce any alteration with regard to the arrangements found for the Y and P atoms; but the oxygen atoms must be arranged in another way if we are to account for the observed maxima.

This is clearly seen from the spectrum of the (111) face. The arrangement given in my previous paper gives, for the amplitudes of the (111) face*,

$$A_n = [2.44 + (-1)^n(1.94 + \cos n\alpha)] \cos \frac{n\pi}{4},$$

which shows that the intensity of the second-order spectrum should vanish independently of the parameter α .

The second-order spectrum, however, does not vanish, but is even found to be stronger than that of the first order.

We must then arrange the oxygen atoms in such a way that the second-order spectrum does not disappear. Following the same line of argument as in the case of zircon†, we find that any tetragonal arrangement of four oxygen atoms round one Y or one P atom will make the second-order spectrum of (111) disappear, and we are, as in the case of zircon, led to suppose that two oxygen atoms are associated with each P atom and two with each Y atom. The axis of the molecular elements must be perpendicular to the C axis.

To obtain a tetragonal arrangement, the molecular axis through one of the face-centred lattices of P or Y must be perpendicular to the axis through the other face-centred lattice of the same element. But with regard to the relative position of the lines through the P atoms to those through the Y atoms, there are, as we saw, two possibilities, which will be apparent by considering the arrangement of lines in a point-plane parallel to the base. If the lines through the Y atoms in this plane were perpendicular to those through the P atoms, we should get an arrangement somewhat different to that of zircon, which would not make the second-order spectrum of (111) disappear. This arrangement, however, would not make the second-order spectrum of this face sufficiently strong as compared with that of the first order.

There seems, indeed, to be no escape from the assumption that the atoms of *xenotime* are arranged in a lattice of the *zircon* type; and we shall see that a proper choice of the parameters will give a satisfactory agreement between

* *Loc. cit.* p. 510, equation (3).

† *Phil. Mag.* xxxii. (1916) p. 77.

the amplitudes calculated from the lattice and those found from the observed intensities.

The arrangement would give a normal spectrum for the (001) face, which is in good agreement with observations. The expressions for the amplitudes of the other four faces are given in equation (12), p. 85, of my second paper. Inserting the values of the atomic numbers, and putting

$$\alpha_1 = 135,$$

$$\alpha_2 = 75,$$

we find the amplitudes given in Table VII.

TABLE VII.

$$\alpha_1 = 135^\circ, \quad \alpha_2 = 75^\circ.$$

| Order. | Face... (111). | | (110). | | (100). | | (101). | |
|--------|----------------|---------|---------|---------|---------|---------|---------|---------|
| | A_L . | A_0 . | A_L . | A_0 . | A_L . | A_0 . | A_L . | A_0 . |
| 1. | 19 | 15 | 100 | 100 | 100 | 100 | 100 | 100 |
| 2. | 35 | 30 | 105 | 121 | 114 | 138 | 87 | 100 |
| 3. | 40 | 40 | 111 | 132 | 135 | 127 | 116 | 95 |
| 4. | 100 | 100 | | | | | | |

A_L is the amplitude calculated from the lattice.

A_0 " " " intensities.

$$A_0 = \sqrt{\frac{I}{k}}.$$

As mentioned in my previous paper, there may be some uncertainty with regard to the value k for the various orders. Even for the same crystal, k may show a different variation with the order number for different faces.

In the previous papers I have put

$$k_1 = 1, \quad k_2 = 0.2, \quad k_3 = 0.07, \quad k_4 = 0.03.$$

In the case of tetramethyl-ammonium iodide, we found that the best agreement was obtained by supposing that k_n did not decrease quite so rapidly with increasing order.

Also in the case of xenotime the values above, as already stated in my previous paper, would give a much too strong first-order spectrum as compared with that of the fourth

order. If, however, we let the values of k decrease somewhat less rapidly, we get a very satisfactory agreement between the amplitudes calculated from the lattice and those calculated from observations. In the present case we have put

$$k_1 = 1.00, \quad k_2 = 2/5, \quad k_3 = 1/7, \quad k_4 = 1/12.$$

When we are going to compare the amplitudes in Table VII., we must remember that only in the case of the faces (111), (110), and (001) was the reflexion obtained from a fairly plane crystal surface. In the case of (100) and (101) we had to measure the reflexion from edges, and as a consequence the intensity measurements will be less accurate. Usually we find in such cases that the intensity of the first order is found too weak, which is also in agreement with our figures. *Thus we arrive at the conclusion that the atoms of xenotime are arranged in a lattice of the zircon type.*

The dimensions of the elementary lattice are the same as given in paper III. Table V. p. 516. We have only to add the distances from the central atom of a molecular element to one of its oxygen atoms. The distance l_Y from the Y atom to one of its oxygen atoms will be

$$l_Y = a \sqrt{2} \frac{\alpha_1}{4\pi} = 2.55 \times 10^{-8} \text{ cm.}$$

And the corresponding distance for the P atoms will be

$$l_P = a \sqrt{2} \frac{\alpha_2}{4\pi} = 1.42 \times 10^{-8} \text{ cm.}$$

Thus, in a "molecular element" the distance from the central atom to one of the two oxygen atoms is much greater in the case of yttrium than in the case of phosphorus, similar to the case of zircon.

§ 8. The fact that the lattice of xenotime is of the same type as that of zircon will have far-reaching consequences with regard to the question between chemical constitution and crystal structure.

From the fact that in zircon we might associate oxygen atoms with each Zr atom, and two oxygen atoms with two Si atoms, we were led to suppose that the zircon mineral had to be considered as a dioxide, ZrO_2SiO_2 .

And in a similar way we were from the structure led to regard rutile as $(\text{TiO}_2)_2$ and kassiterite as $(\text{SnO}_2)_2$.

Now, however, we have found that the atoms of xenotime (YPO_4), in spite of the difference of valency of the elements,

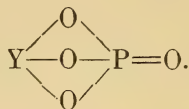
are arranged in a lattice of the zircon type; but are we, then, to draw the conclusion that also xenotime is to be given a constitution formula, YO_2PO_2 ? I think not, in the usual meaning of the word, although we found * that the geometry of the zircon lattice would indicate that in a "molecular element" MO_2 oxygen atoms probably were attached to the central atom M in another way to that in which they were attached to the other neighbouring atoms.

Indeed, it will be difficult to prove anything so long as we do not know exactly what realities are to be associated with a constitution formula and with the conception of valency.

Probably our ideas in this respect will have to be fundamentally changed.

A constitution formula serves to express certain chemical properties of the substance, but it may not at all be able to express the true relation in space of the atoms which constitute the molecule.

Let us return to our case of xenotime, and assume it is to be considered as a phosphate, the constitution formula of which should be



This formula would put one of the oxygen atoms into a singular position; and if the valency units are to indicate forces, the Y atoms would be attached to the P atoms, as far as chemical attraction is concerned, only by means of the oxygen atoms.

Comparing the constitution formula with the arrangement found for the atoms in the solid substance, we see that the constitution formula does not give any indication of the true arrangement. Thus there is no oxygen atom which takes up any singular position, and the oxygen atoms seem to be associated in a similar way with both Y and P.

A constitution formula which should express the way in which the atoms are arranged in the crystal—or the *constitution of the solid form*—should be written YO_2PO_2 .

This result may be best expressed by saying that the constitution formula of the solid structure and the constitution formula giving the chemical properties may be two different things; and we cannot, from the atomic arrangement, find out the "chemical constitution" of the substance.

* Phil. Mag. xxxii. p. 92.

We have previously found that the constitution of the solid state of zircon, rutile, and kassiterite should be ZrO_2SiO_2 , $(\text{TiO}_2)_2$, and $(\text{SnO}_2)_2$; but, from what we have said, we should not from these formulæ be able to conclude that they were adequate expressions for the chemical properties of the substances.

If we assume xenotime to be a phosphate, we might equally well suppose that these substances were to be considered as silicate, titanate, and stannate from the point of view of chemical properties.

Another way of putting it would be to say that the constitution formula varies with the state of the substance.

The ordinary chemical constitution formula is intimately related to the idea of a molecule; but in the crystalline state the idea of a molecule as an individual system has lost its significance. In certain cases it may be convenient for the description of the structure in quite a formal way to regard molecular elements, but they must not be supposed to be real individual molecules. The forces connecting neighbouring atoms of different molecular elements may be equally strong and of essentially the same nature as those existing between the atoms of the same molecular element*.

And when the idea of molecules loses its meaning, it is really no wonder that the chemical constitution formula ceases to express the structure of solids.

In the liquid and gaseous state, however, we have to do with individual molecules, or molecules dissociated into ions; and it may be possible that in these states the atoms would arrange themselves more in agreement with the chemical constitution formula. This may also be very likely to occur, on account of the fact that the chemical reactions which determine the chemical constitution mostly take place in aqueous or gaseous systems.

As the result of our reasoning, we might say that the substances belonging to the zircon group—xenotime included—

* If we suppose that in a solid the atoms are not connected up into molecules, the whole lattice structure will be kept together by the same kind of forces as those which are engaged in the chemical binding of the atoms of a molecule; in other words, the elastic forces of a solid body should be intimately related to the affinity forces which constitute the attraction between atoms.

Now the forces engaged in the binding of the atoms of a molecule are much greater than the forces by which the molecules of a liquid are kept together, and thus we see that the structure of the crystals gives a natural explanation of the great increase in the elastic forces which accompany the passage of a substance from the liquid to the solid state.

in the crystalline state have a structure corresponding to a formula $M_1O_2M_2O_2$, which we might call the constitution formula of the solid state; but this constitution formula may be quite different from the chemical constitution formula of the substances, or from the constitution of the liquid, gaseous, or ionic form. Thus the chemical constitution of xenotime may be that of a phosphate, and zircon may have the chemical constitution of a silicate; but we must also be aware of the possibility that identity of crystal structure does not involve identity or similarity of chemical constitution. Thus, if we regard xenotime as a phosphate, we need not regard zircon as a silicate or rutile as a titanate.

In conclusion, I want to express my indebtedness to Mr. H. Schjelderup for his valuable assistance during these researches. My thanks are also due to Miss Liv Gleditsch for making the models which are reproduced in this paper.

University of Christiania,
January 1, 1917.

XLI. *Osmotic Pressure: its Relation to the Membrane, the Solvent, and the Solute.* By FRANK TINKER, D.Sc.*

IT is a noteworthy fact that whereas most of the kinetic explanations of the mechanism of osmotic pressure have focussed an almost exclusive attention on the solute, the thermodynamic cycle by which the osmotic laws are derived is carried out with the solvent, and with no reference to the solute as distinct from the solution †. For this reason it has come to be generally recognized, at least by those who during recent years have treated the subject thermodynamically, that the osmotic mechanism is to be explained ultimately in terms of the solvent rather than the solute; osmotic flow, for instance, takes place because the potential of the pure solvent is greater than the potential of the solvent inside the solution. Experiment also lends strong support to this view. With the exception that moisture travels across a semipermeable membrane in a much more condensed condition than vapour proper, the phenomenon of osmotic

* Communicated by Sir Oliver Lodge, F.R.S., being part of a Thesis approved for the Degree of Doctor of Science in the University of London.

† I refer to the process in which the osmotic pressure is first obtained in terms of the vapour pressure by the formula $P = \frac{RT}{V} \log \frac{p}{p'}$, and then afterwards in terms of the concentration by combining this formula with Raoult's law $\frac{p}{p'} = \frac{N+n}{N}$.

flow is very similar to that of vapour flow; diffusion proceeds from pure solvent to solution because the pure solvent induces a greater pressure and concentration inside the membrane than the solution does*.

In the present paper the subject of osmosis is developed quantitatively from the above basis; and the osmotic pressure connected with the conditions inside the pure solvent, the solution, and the membrane. But inasmuch as for this purpose the Dieterici equation of state is largely employed, it is to be noted at the outset that the results obtained by the application of this equation are only of value in so far as it represents accurately the conditions inside fluids. The equation in its various forms has, however, been applied to fluids with such a measure of success that the formulæ developed herein are in all probability at least approximately accurate†.

NOTATION.

| | |
|--|------------|
| Liquid pressure (<i>i. e.</i> pressure inside liquid) | π |
| Vapour pressure | p |
| Pressure inside semipermeable membrane | ρ |
| Hydrostatic pressure | Π |
| Osmotic pressure | P |
| Molecular volume | V |
| Work done during evaporation of 1 mol. into vapour phase proper | A |
| Work done during evaporation of 1 mol. into semipermeable membrane | B |
| Expansion on solution (per solute molecule dissolved) | ϵ |
| Coefficient of compressibility | β |
| Heat of dilution | Q |
| Number of molecules of solvent in solution | N |
| Number of molecules of solute in solution | n |

In addition the suffix 1 is used for the solvent (*e. g.* V_1 = mol. vol. of pure solvent) and the suffix 2 for the solute.

Partial pressures, volumes, &c. (in solution) are indicated by dashed symbols.

When it is necessary to consider the volume as a function of the hydrostatic pressure, an additional suffix is used. Thus $V_{1(a)}$ represents the molecular volume of pure solvent under the atmospheric pressure a .

The Dieterici equations employed are:—

for the pressure in the interior of the liquid

$$\pi(V - b) = RT;$$

for the external vapour pressure

$$p = \pi e^{-\frac{A}{RT}} = \frac{RT}{V - b} e^{-\frac{A}{RT}}.$$

* Tinker, Proc. Roy. Soc. Contemporary number.

† For the fundamental ideas underlying the Dieterici equation and its application to the determination of the vapour pressures of binary mixtures, the reader is referred to a previous paper by the author. Phil. Mag. xxxii. Sept. 1916, p. 295.

1. THE PROCESSES OPERATIVE DURING SOLUTION.

It is obvious that when two fluids are mixed together without appreciable total volume change, each component of the mixture separates the molecules of the other component from one another. An immediate consequence of this fact is that the partial pressures and concentrations of the two components are less in the mixture than in the pure substances themselves*, and if either component is capable of "evaporating" from the mixture into another phase, its partial pressure in that phase is also reduced. It is thus not necessary to assume, as some have done†, that the lowering of the vapour pressure of the solvent by the process of solution is due to solvation, or even to the blocking by the solute molecules of solvent molecules which would otherwise evaporate‡. It is the reduction in the pressure and concentration of the solvent inside the solution which causes the lowering of the vapour pressure, whilst solvation and other solution effects which also occur are the cause of abnormalities in the reduced vapour pressure rather than the primary cause of the reduction itself.

The present section is a development of the theory of fluid mixtures from the fundamentals of the kinetic theory. The treatment has been made as broad and general as possible so that it can be extended to solutions of any strength. The only assumptions made are the following:—

- (i.) The pressure of any component inside a fluid mixture is inversely proportional to the free space available to each molecule of that component, *i. e.* it is inversely proportional to the

$$\left(\frac{\text{total free space in a given vol.}}{\text{no. of mols. of the component in the given vol.}} \right).$$

- (ii.) The exact relationship between the partial pressure of the component and the free space available to its molecules is given by the equation,

$$\text{partial pressure} \left(\frac{\text{total free space in given vol.}}{\text{no. of mols. of compt. in given vol.}} \right) = RT.$$

* The simplest and most obvious case is that of mixing two gases without total volume change. Thus, if one volume of gas A at atmos. press. is mixed with 1 vol. gas B also at atmos. press. to give 2 vols. of mixture also at atmos. press., the partial pressures of A and B are only half the pressures inside pure A and B.

† Poynting, *Phil. Mag.* (5) xlii. p. 298 (1896); Callendar, *Proc. Roy. Soc. A.* xc. (1908); Dolezalek, *Zeit. Phys. Chem.* lxxxiii. p. 40 (1913), and other papers.

‡ Lowry, *Phil. Mag.* (6) xiii. p. 552 (1897).

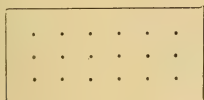
It is to be noted also that these assumptions are only valid for the interior of the fluid * ; but it is immaterial whether the fluid be the solution itself, the vapour phase proper, the membrane or any other medium in contact with the solution. To prevent the subject from becoming unduly complicated, it is also assumed that neither the solvent nor the solute is either associated or dissociated, and that no solvates are formed.

(a) *The Partial Pressures of Solvent and Solute inside the Solution.*

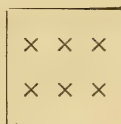
Let N mols. of a solvent X having an internal fluid pressure π_1 be mixed with n mols. of a solute Y having a fluid pressure π_2 so as to give a mixture of $(N+n)$ mols. having a total fluid pressure π . During the mixing, both of the constituents X and Y will expand into one another until the pressure throughout the mixture is uniform, *i. e.* until "the mean free space F per molecule of either kind" is the same for each molecule, whether of X or of Y †. Or, using an alternative phraseology, on mixing, the molecular volumes V_1 and V_2 of the pure solvent and solution both alter themselves in such a way that (V_1-b_1) and (V_2-b_2) readjust themselves to a common volume which can be represented either by $V_1'-b_1$ or $V_2'-b_2$, or by the letter F .

* This is, of course, one of the fundamental Dieterici assumptions. The Dieterici equation for the pressure in the interior of a pure fluid is $\pi(V-b)=RT$.

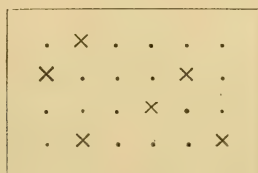
† For this phrase I am indebted to Prof. A. W. Porter, F.R.S. The conditions before and after mixing can be represented graphically, as below :—



N mols. of pure solvent
at press. π_1 .



n mols. of pure solute
at press. π_2 .



$(N+n)$ mols. of solution at press. π .
Mean free space F the same for each molecule.

We then have

Total free space in mixture

$$= (N+n)F = (N+n)(V_1' - b_1) = (N+n)(V_2' - b_2). \quad [1]$$

Employing the equation postulated in the second assumption, we get immediately for the partial pressure π_1' of the solvent inside the solution

$$\pi_1' \frac{(N+n)}{N} F = RT,$$

and for the pressure π_1 inside the pure solvent

$$\pi_1(V_1 - b_1) = RT,$$

and hence

$$\frac{\pi_1'}{\pi_1} = \frac{N}{N+n} \cdot \frac{V_1 - b_1}{F} \dots \dots \dots [2]$$

Similarly, for the partial pressure π_2' of the solute inside the solution

$$\frac{\pi_2'}{\pi_2} = \frac{n}{N+n} \cdot \frac{V_2 - b_2}{F} \dots \dots \dots [3]$$

The equations [2] and [3] can be developed further by considering in detail the volume changes which take place on mixing.

Let the increase in the total volume* on mixing be $n\epsilon$ (ϵ can be looked on as the expansion of the total volume per molecule of solute added). We have

$$\text{Total volume of solution} = NV_1 + nV_2 + n\epsilon,$$

$$\text{Total free space in solution} = N(V_1 - b_1) + n(V_2 - b_2) + n\epsilon.$$

But the total free space in solution is also $= (N+n)F$.

Hence

$$\begin{aligned} (N+n)F &= N(V_1 - b_1) + n(V_2 - b_2 + \epsilon) \\ &= (N+n)(V_1 - b_1) - n\{(V_1 - b_1) - (V_2 - b_2 + \epsilon)\}. \end{aligned}$$

Dividing throughout by $(N+n)(V_1 - b_1)$, we get

$$\frac{F}{V_1 - b_1} = 1 - \frac{n}{N+n} \left(1 - \frac{V_2 - b_2 + \epsilon}{V_1 - b_1} \right) \dots \dots [4]$$

* *I. e.* the excess of the volume of the solution over the sum of the volumes of the two components. It is to be noted that ϵ varies with the pressure to which the solution is subjected; and that V_1' and V_2' are also variable with the pressure. But since in the present paper no pressures are ever put on the pure solvent or solute, V_1 and V_2 are regarded as being constant and equal to the molecular volumes at atmospheric pressure.

Substituting in equation [2] we have

$$\begin{aligned}\frac{\pi_1}{\pi_1'} &= \frac{N+n}{N} \left\{ 1 - \frac{n}{N+n} \left(1 - \frac{V_2 - b_2 + \epsilon}{V_1 - b_1} \right) \right\} \\ &= \frac{N+n}{N} - \frac{n}{N} \left(1 - \frac{V_2 - b_2 + \epsilon}{V_1 - b_1} \right) \dots \dots \dots [5]\end{aligned}$$

Similarly,

$$\frac{\pi_2}{\pi_2'} = \frac{N+n}{n} - \frac{N}{n} \left(1 - \frac{V_1 - b_1 + \frac{n}{N}\epsilon}{V_2 - b_2} \right) \dots \dots \dots [6]$$

Equations [2], [3], [4], [5], [6] are general, and hold whatever volume changes may take place in either the partial volumes or the total volume.

Equations [2] and [3] show that the partial liquid pressures of the solvent and solute are determined partly by their respective molar fractions and partly by the changes in molecular volume which take place on mixing.

The most important particular case is the one in which we get the partial pressure of the solvent given by the relation

$$\frac{\pi_1'}{\pi_1} = \frac{N}{N+n}^*.$$

It is evident from equation [2] that the relationship can hold only if $V_1 - b_1 = F = V_1' - b_1$, *i. e.* if $V_1' = V_1$; in other words, the partial vapour pressure ratio $\frac{\pi_1'}{\pi_1}$ for the solvent is equal to the molar fraction $\frac{N}{N+n}$ only when the molecular volume of the solvent undergoes no change by the process of solution. It can be shown, however, that all dilute solutions under normal conditions obey the relationship

$$\frac{\pi_1'}{\pi_1} = \frac{N}{N+n}$$

more or less approximately †. Consider, for instance, a litre

* As will be shown later, the simple osmotic laws for dilute solutions hold only when the above relationship holds.

† It is important to note the limitation of "normal conditions." The partial pressures, both inside the solution and in the vapour phase proper, &c., vary with the hydrostatic pressure placed on the solution. It will be shown subsequently that with ideal solutions, for instance, at osmotic equilibrium, π_1' and π_1 are equal instead of π_1 being greater than π_1' as under normal conditions.

of any deci-normal aqueous solution *, and, as an extreme case let

$$(V_2 - b_2 + \epsilon) = 10(V_1 - b_1) \quad \{\text{cf. equation [5]}\}.$$

We have

$$n = \frac{1}{10}, \quad N = 55.5, \quad \frac{n}{N} \left(1 - \frac{V_2 - b_2 + \epsilon}{V_1 - b_1} \right) = -\frac{1}{60} \text{ approx}$$

$$\text{and} \quad \frac{N+n}{N} = 1 \text{ approx.}$$

The error in counting $\frac{\pi_1'}{\pi_1} = \frac{N}{N+n}$ is thus $\frac{1}{60}$ on unity, or less than 2 per cent. The magnitude of the error is evidently determined by the number of solute molecules added to the solvent. If not many are added, their influence on the mean free space F in the solution is overwhelmed by the influence of the solvent, so that the internal conditions inside the solvent remain more or less unchanged.

We must not, however, suppose that because the *solvent* undergoes no appreciable volume change in the case of dilute solutions, the solute also undergoes no volume change, and also that the total volume change is zero. Both these latter hypotheses are in contradiction both to theory and experiment †. The solute, for instance, has to change its molecular volume in such a way that $(V_2 - b_2)$ alters itself to $(V_2' - b_2) = F = (V_1' - b_1)$ { $= (V_1 - b_1)$ for dilute solutions }, *i. e.* on adding the solute to the solvent, in the case of dilute solutions, the free space of the solute readjusts itself to that of the pure solvent; whence the molecular volume of the solute also alters from V_2 to $(V_1 - b_1 + b_2)$. In the same way it can be shown by developing the equation [4], that the total expansion $n\epsilon$ on mixing is given by the relation

$$n\epsilon = n\{(V_1 - b_1) - (V_2 - b_2)\} - (N+n)(V_1 - V_1'). \quad [7]$$

The total volume change becomes zero in two cases only :

- (a) when $(V_1 - b_1) = (V_2 - b_2)$ and $V_1' = V_1$ simultaneously, *i. e.* when the original "free spaces" of pure solvent and solute are equal and undergo no volume change on mixing ;
- (b) when

$$(N+n)(V_1 - V_1') = n\{(V_1 - b_1) - (V_2 - b_2)\}$$

$$\text{or} \quad V_1 - V_1' = \frac{n}{N+n} \{(V_1 - b_1) - (V_2 - b_2)\}.$$

* A solution is usually taken as dilute up to a strength of $\frac{N}{10}$.

† It is well known that a slight total volume change on solution is the rule, even with very dilute solutions. For a comprehensive set of determinations see Cameron & Robinson, Journ. Phys. Chem. xiv. p. 1 (1910).

It is evident that either of these conditions will be satisfied but rarely. In the case of dilute solutions (in which $V_1' = V_1$) equation [7] indicates that the total volume change

$$n\epsilon = n\{(V_1 - b_1) - (V_2 - b_2)\}.$$

There will thus be an expansion or contraction on mixing according as $(V_1 - b_1)$ is greater or less than $(V_2 - b_2)$ *.

(b) *The Partial Pressures of the Solvent and Solute in the Vapour Phase.*

By combining the Dieterici equation with the foregoing results we can arrive at the laws obeyed by the solvent and solute in any other phase with which the solution is in contact and into which either (or both) solvent or solute can diffuse. The equation connecting the pressure of the solvent and solute in any phase with the pressure inside the solution can be written as

$$p' = \pi' e^{-\frac{A'}{RT}}, \quad . \quad . \quad . \quad . \quad . \quad [8]$$

where p' and π' are partial pressures in the phase and solution respectively, and A' is the work done in transferring a molecule from the solution to the phase in question.

We thus have for the partial pressure of the solvent p_1' in any phase (say the vapour phase) †

$$\frac{p_1}{p_1'} = \frac{\pi_1 e^{-\frac{A_1}{RT}}}{\pi_1' e^{-\frac{A_1}{RT}}} = \frac{\pi_1}{\pi_1'} e^{\frac{\partial A}{RT}} = \left\{ \frac{N+n}{N} - \frac{n}{N} \left(1 - \frac{V_2 - b_2 + \epsilon}{V_1 - b_1} \right) \right\} e^{\frac{\partial A_1}{RT}}, \quad . \quad . \quad . \quad . \quad . \quad [9]$$

∂A_1 being the excess work performed by "evaporating" one molecule of the solvent from the solution into the phase over the work performed when the solvent is "evaporated" from the pure solvent.

We can extend the applicability of equations [8] and [9] by first proving that ∂A_1 is approximately equal to the heat of dilution Q of the solution.

Let the pure solvent and the solution be separated from one another by the phase in question †. A molecule of solvent can be conveyed from the pure solvent to the

* In the absence of solvation and association and dissociation changes this deduction should be capable of experimental test. The fact that physical factors only can cause total volume change invalidates many determinations of the formulæ of the "hydrates" formed during solution from the volume changes which take place on mixing.

† It is immaterial what this phase is. It may be either a vacuum (the vapour phase proper), a colloidal membrane, or another liquid or solid in which the solvent and solute are soluble.

solution irreversibly, and without the performance of external work, in two ways :

- (i.) It can be allowed to diffuse into the phase in question first, to then expand inside the phase from the pressure p_1 to the pressure p_1' , and lastly allowed to diffuse from the phase into the solution. The total heat given out by this process is $\partial A_1 + U$, where U is the diminution in the internal energy of the solvent during the expansion from p_1 to p_1' .
- (ii.) It can be added directly to the solution, with a total heat evolution Q , where Q is the heat of dilution.

Hence, since the total heat effect is independent of the path traversed, we have $\partial A_1 + U = Q$.

For the vapour phase proper, at any rate, we can neglect U so that $\partial A_1 = Q$ (approx.).

Equation [9] can thus also be written

$$\frac{p_1}{p_1'} = \left\{ \frac{N+n}{N} - \frac{n}{N} \left(1 - \frac{V_2 - b_2 + \epsilon}{V_1 - b_1} \right) \right\} e^{\frac{Q}{RT}}. \quad [10]$$

If the heat of dilution of the solution is small compared with RT (as it usually is) the equation becomes

$$\frac{p_1}{p_1'} = \left\{ \frac{N+n}{N} - \frac{n}{N} \left(1 - \frac{V_2 - b_2 + \epsilon}{V_1 - b_1} \right) \right\} \left(1 + \frac{Q}{RT} \right). \quad [11]$$

Equation [10] and its approximate form (equation 11) are the general equations for the vapour pressure of a solution of any non-volatile solute at any concentration, it being assumed that neither the solvent nor the solute is associated or dissociated.

For the *dilute* solution the equation becomes *

$$\begin{aligned} \frac{p_1}{p_1'} &= \frac{N+n}{N} \left(1 + \frac{Q}{RT} \right) \\ \text{or} \quad \frac{p_1'}{p_1} &= \frac{N}{N+n} \left(1 - \frac{Q}{RT} \right). \quad \dots \dots [12] \end{aligned}$$

(c) *Ideal and Non-Ideal Solutions.*

The ideal solution may be defined as one whose partial vapour pressure under ordinary conditions is given by the equation

$$\frac{p_1'}{p_1} = \frac{N}{N+n} \dagger.$$

* *Supra*, the approximate equation $\frac{\pi_1'}{\pi_1} = \frac{N}{N+n}$ given on p. 433.

† Cf. Willard Gibbs, 'Nature,' lx. p. 46 (1897); Van Laar, *Zeit. Phys. Chem.* xv. p. 457 (1894).

For this relationship to hold it is evident from equation [9] that (i.) the heat of dilution of the solution must be zero, and (ii.) the partial pressure of the solvent inside the solution shall be given by the equation

$$\frac{\pi_1'}{\pi_1} = \frac{N}{N+n}.$$

The latter condition is only fulfilled if the solvent undergoes no volume change during the process of solution (*vide* p. 433). As is shown on p. 433, dilute solutions in general satisfy the latter relationship. We must not, however, infer that all dilute solutions are ideal. Equation [12] shows that they are only ideal if they have no heat of dilution. In the case of dilute sulphuric acid solutions, for instance (Q being positive), the vapour pressures are abnormally low*, whilst dilute aqueous phenolic solutions have a partial water vapour pressure which is almost equal to that of pure water†.

Conversely, we may define non-ideal solutions as those which do not satisfy the relationship

$$\frac{p_1'}{p_1} = \frac{N}{N+n}.$$

It is evident that departure from ideality in the cases we have been dealing with are caused by‡:

- (i.) Volume changes of the solvent during the process of solution; these volume changes are caused by the fact that the free space (and intrinsic pressure) of the pure solute is generally different from that of the pure solvent, so that the solvent has to accommodate itself to the solute when the two are mixed together; and
- (ii.) Heat effects on dilution. The vapour pressure tends to be abnormally high or low according as the solution has a negative or positive heat of dilution.

The general equation for the vapour pressure of non-ideal solutions is [10].

* Cf. the figures given by Regnault, *Ann. Chim. Phys.* (3) xv. p. 179 (1845); Sorel, *Zeit. angew. Chem.* p. 272 (1889).

† Schreinemakers, *Proc. Roy. Soc. Amsterdam*, vol. iii. pp. 1 & 701.

‡ *I. e.* with solutions in which the solvent and solute are neither associated nor dissociated, and in which there are no solvates formed. Evidently these latter effects, if they are present, will cause still greater deviations from ideality.

2. THE PHENOMENA OF OSMOTIC FLOW.

Consider a semipermeable membrane having a thickness sufficiently great for it to be regarded as a separate phase in the osmotic system*. Let the pure solvent be on one side of the membrane and the solution on the other. The solvent tends to diffuse into the membrane from both the pure solvent and the solution; a pressure ρ_1 (say) tending to be generated within the membrane by the pure solvent and a pressure ρ_1' (say) by the solution. From equation [9]

$\frac{\rho_1}{\rho_1'}$ is given by the equation

$$\frac{\rho_1}{\rho_1'} = \frac{\pi_1}{\pi_1'} e^{\frac{B_1' - B_1}{RT}} = \left\{ \frac{N+n}{N} - \frac{n}{N} \left(1 - \frac{V_2 - b_2 + \epsilon}{V_1 - b_1} \right) e^{\frac{\partial B_1}{RT}} \right\}, [13]$$

where ∂B_1 is the excess of the latent heat of vaporization of the solvent from the pure solvent into the membrane over the heat of vaporization of the solvent from the solution into the membrane†.

It is evident that the solvent will flow from the pure solvent to the solution if the pressure ρ_1 generated in the membrane by the pure solvent is greater than the pressure ρ_1' generated in the membrane by the solvent which is in the solution.

That this will almost invariably be the case under normal conditions can be shown as follows. Developing equation [13] we get

$$\begin{aligned} \frac{\rho_1 - \rho_1'}{\rho_1'} &= \left\{ \frac{N+n}{N} - \frac{n}{N} \left(1 - \frac{V_2 - b_2 + \epsilon}{V_1 - b_1} \right) \right\} e^{\frac{\partial B_1}{RT}} - 1 \\ &= \frac{n}{N} \left(\frac{V_2 - b_2 + \epsilon}{V_1 - b_1} \right) e^{\frac{\partial B_1}{RT}} \text{ (approx.), } \dots [14] \end{aligned}$$

since $e^{\frac{\partial B_1}{RT}}$ does not usually differ very much from unity.

Now, in practice, $e^{\frac{\partial B_1}{RT}}$ is always positive, whether ∂B_1 is positive or negative, for ∂B_1 , which is usually negligible, is of a much less order of magnitude than RT . Also $(V_2 - b_2 + \epsilon)$ is positive, except in the unlikely case in which the total expansion (ϵ) per solute molecule dissolved is negative and actually greater than the free space $(V_2 - b_2)$ of the solute itself. Hence $\rho_1 - \rho_1'$ will almost invariably be positive, so

* The actual colloidal membranes satisfy this condition.

† The heat evaporation into the membrane is obviously not the same as that into the vapour phase proper. It is clear, however, from the general nature of the proof on p. 435 that the equations for ρ are similar to those for p .

that ρ_1 will be greater than ρ_1' . This explains why osmotic flow usually takes place from pure solvent to solution. The pure solvent generates a greater solvent pressure inside the membrane than the solution does.

We must not, however, suppose that the solvent *of necessity* always flows from pure solvent to solution. It would flow the other way if for any reason the partial pressure* generated in either the membrane or the vapour phase proper by the solution were greater than the pressure generated by the pure solvent itself. It is not unlikely that solutions of ordinary phenol, which apparently under certain conditions have a partial water vapour pressure greater than the vapour pressure of pure water itself†, come under this category. Prof. Adrian Brown and the present author have proved that the phenolic solutions in general are very abnormal in their osmotic behaviour‡.

In this connexion it is also interesting to note the effect of compressing the solution whilst leaving the pure solvent under atmospheric conditions. It is evident that the shrinkage caused by compression will tend to make ϵ negative, so that ultimately, by the application of a pressure great enough ($V_2 - b_2 + \epsilon$) will become negative. When this occurs ρ_1 will become less than ρ_1' and the solvent will flow from the solution to the pure solvent. This is actually what happens when a pressure greater than its osmotic pressure is applied to the solution.

Let us now consider the causes for the abnormalities in the phenomena of osmotic flow; and let us confine attention in the first place to the case in which two dilute solutions of different solutes, having equal concentrations and under the same external hydrostatic pressure, are on opposite sides of the membrane. If ρ_1' and ρ_1'' are the solvent pressures generated in the membrane in each case we have from the equation [12]

$$\frac{\rho_1' - \rho_1''}{\rho_1} = \frac{N}{N+n} \left(\frac{Q'' - Q'}{RT} \right), \quad \dots \quad [15]$$

where Q' and Q'' are the heats of dilution of the two solutions. Similarly, for the vapour pressures proper, we have

$$\frac{p_1' - p_1''}{p_1} = \frac{N}{N+n} \left(\frac{Q'' - Q'}{RT} \right). \quad \dots \quad [16]$$

* *I. e.* "Partial pressure of the solvent."

† Schreinemakers, *loc. cit.* p. 14 (footnote).

‡ Proc. Roy. Soc. B. lxxxix. p. 119 (1915).

From equations [15] and [16] we can derive three possible cases:—

- (i.) If both of the dilute solutions are ideal and have zero heat of dilution, then $\rho_1'' = \rho_1'$ and $p_1' = p_1''$. Two ideal solutions of equal concentration are thus in osmotic equilibrium with one another, and there will be no osmotic flow from the one to the other.
- (ii.) If one solution is ideal and the other is not, the system is not in equilibrium, although the concentrations of the two solutions may be equal. The flow will be from the ideal solution to the non-ideal solution, according as to the heat of dilution of the non-ideal solution is positive or negative.
- (iii.) If both solutions are non-ideal, osmotic equilibrium is possible only when the two heats of dilution are equal. In any other case osmotic flow will take place from the solution having the lesser heat dilution to the solution having the greater.

By virtue of the relationships which have been established in the foregoing pages between the heat of dilution and the heat of vaporization, either into the membrane or into the vapour phase proper, the above case of osmotic flow for non-ideal solutions can be elaborated in somewhat more detail.

Thus, since $Q = \partial A_1 = \partial B_1$ (*loc. cit.* p. 12), we can write

$$Q'' - Q' = A_1'' - A_1' = B_1'' - B_1'.$$

Hence, we may also state that the osmotic flow will take place from the solution having the lower value of A_1' to that having the higher value of A_1' . Since A_1' is a function of the intrinsic pressure which increases with the latter*, and consequently also with the surface-tension†, we arrive at the further result that the flow will take place from the solution having the lower intrinsic pressure and surface-tension to that having the higher intrinsic pressure and surface-tension. Herein comes the application of the “intrinsic pressure” and surface-tension theory of osmosis which I. Traube has advocated so vigorously on empirical grounds‡. The preceding analysis shows that the theory

* This is an immediate deduction from the Laplace theory of capillarity. It is in agreement with experiment also, since liquids which have a high intrinsic pressure have also a large latent heat. (*Cf.* W. C. McC. Lewis, *Trans. Faraday Soc.* April 1911.)

† A liquid which has a high intrinsic pressure and latent heat has also a high surface-tension.

‡ *Journ. Phys. Chem.* xiv. p. 452 (1910) and other papers. Traube has correlated surface-tension, vapour pressure, intrinsic pressure, &c., with their effect on osmotic flow.

must be limited to the case in which two non-ideal dilute solutions of equal concentration are placed on opposite sides of the membrane. Subject to this limitation Traube's surface-tension theory will no doubt continue to be of great value, even as it has proved to be in the past. The scope of Traube's theory, limited as above, would apparently be extensive*, for most actual solutions are more or less non-ideal.

We can now sketch briefly the general theory of osmotic flow. It is evident that if two solutions (each under the same hydrostatic pressure) are on opposite sides of a membrane, the solvent will flow from the one which generates the greater pressure † inside the membrane, *i. e.* from the one which has also the greater partial (solvent) vapour pressure. Now, the pressure generated by each solution in either the membrane or the vapour phase proper is determined partly by the liquid pressure π_1' of the solvent inside the solution and partly by the work factor A_1' ; so that we can regard the magnitude and direction of osmotic flow as being caused ultimately by differences in the value of π_1' and A_1' for the two solutions. If the differences in the value of A_1' are nil, the osmotic flow is thus determined entirely by the differences in π_1' , the direction of the flow obviously proceeding from the solution in which the solvent has the higher fluid pressure to the one in which it has the lower fluid pressure ‡. If, on the other hand, the differences in π_1' are eliminated, as by working with dilute solutions of equal concentration on opposite sides of the membrane, the direction of flow is determined entirely by the differences in the value of A_1' , *i. e.* (and as shown above) by the differences in heats of dilution, intrinsic pressure, surface-tension, &c.

The problem can be resolved even still further. The pressure of the solvent inside a solution is itself determined by its molar fraction and also by the change in volume which it undergoes during the process of solution (equation [2] p. 432); so that in the general case we can state that the

* *Cf.* Macallum, *Brit. Assoc. Reports*, 1910, p. 740. It is clear also that in the case we have been considering the *velocity* of osmosis will be determined largely by intrinsic pressure (and surface-tension) differences between the two solutions. In this connexion it is interesting to note that Prof. Adrian Brown and the author have found that the rate of osmotic flow into barley seeds becomes greater as the surface-tension of the outside solution diminishes. (*Proc. Roy. Soc. B.* lxxxix. p. 119 (1915).)

† *I. e.* partial pressure of the solvent.

‡ Tinker, '*Nature*,' xcvii. p. 122 (1916). This idea of osmosis being determined by magnitude of the fluid pressure of the solvent seems to have been foreshadowed by Porter (*Proc. Roy. Soc. A.* lxxx. p. 457 (1908), Addendum to paper).

magnitude and direction of osmotic flow is ultimately determined, partly by the relative concentrations of the two solutions, partly by their relative heats of dilution, surface-tensions, intrinsic pressures, &c., and partly by the relative magnitude of the volume changes which the solvent undergoes during the process of solution. If, on the one hand, we eliminate surface-tension and intrinsic pressure differences, &c., by working with two ideal solutions on opposite sides of the membrane, the direction of flow is invariably from the weaker solution to the stronger one. If, on the other hand, we eliminate concentration differences and work with two non-ideal dilute solutions of equal strength, the direction of flow is (as shown above) from the solution having the lower heat of dilution, surface-tension, intrinsic pressure, &c., to that having the higher value of these quantities; in fact, Traube's theory of osmosis holds good. Whilst if we eliminate both concentration and surface-tension differences, &c., by working with two equally strong non-ideal solutions having equal heats of dilution, the direction of flow will be towards the solution in which the solvent has undergone the greater expansion during the process of solution.

3. THE CONDITIONS AT OSMOTIC EQUILIBRIUM.

Consider again the case in which pure solvent and solution are separated by a semi-permeable membrane which is thick enough to be regarded as a separate phase in the osmotic system *. Let the pure solvent be under the atmospheric pressure a , and the solution under such a hydrostatic pressure P that the solvent and solution are in osmotic equilibrium.

(a) *Relationship between the Pressure of the Solvent in the various parts of an Osmotic System, the latter being at Equilibrium.*

It is evident that, when a system is at osmotic equilibrium, the pressure ($\rho_1'_{(P)}$) generated inside the membrane by the solution must be equal to the pressure ($\rho_{1(a)}$) generated by the pure solvent, just as the vapour pressures proper of pure solvent and solution are equal at osmotic equilibrium †.

* Footnote (*) on p. 438.

† Thomson & Poynting, 'Properties of Matter,' p. 191. A. W. Porter, Proc. Roy. Soc. A. lxxix. p. 519 (1907), *ibid.* A. lxxx. p. 457 (1908). The ultimate proof of both the theorems mentioned is very simple. If the pressure were not uniform in either the membrane or in the vapour phase proper, a process of diffusion would take place. The fact that work could be obtained from the process can be made to contradict the second law of thermodynamics.

Starting from inside the membrane, and travelling outwards into pure solvent and solution respectively through the surface film between the membrane and the liquid in each case, let us now apply the Dieterici equation in its simplest form.

For the pressure $\pi_{1(a)}$ inside the pure solvent we have

$$\pi_{1(a)} = \rho_{1(a)} e^{\frac{B_1}{RT}}.$$

„ „ $\pi_{1'(P)}$ of the solvent inside the solution we have

$$\pi_{1'(P)} = \rho_{1'(P)} e^{\frac{B_1'}{RT}},$$

where B_1 and B_1' have a similar meaning to A_1 and A_1' , referring, however, to evaporation into the membrane. Hence, since $\rho_{1'(P)} = \rho_{1(a)}$ (see above), we get

$$\frac{\pi_{1'(P)}}{\pi_{1(a)}} = e^{\frac{B_1' - B_1}{RT}} = e^{\frac{\partial B}{RT}} = e^{\frac{Q}{RT}}*,$$

whence

$$\pi_{1'(P)} = \pi_{1(a)} e^{\frac{Q}{RT}} = \pi_{1(a)} \left(1 + \frac{Q}{RT}\right) \text{ (approx.)}. \quad [17]$$

From this equation [17] it appears that, if the solution is an ideal one with zero heat of dilution, at osmotic equilibrium the pressure $\pi_{1'(P)}$ of the solvent inside the solution is equal to the pressure $\pi_{1(a)}$ of the solvent inside the pure solvent. When therefore the solution has no heat of dilution, we can lay down the fundamental generalization that at osmotic equilibrium *the pressure of the solvent is uniform in similar phases throughout the whole osmotic system*. The pressure of the solvent throughout the vapour phase is uniform; it is also uniform throughout the membrane; whilst the pressure of the solvent inside the solution is equal to that inside the pure solvent. The generalization breaks down, however, in the case of non-ideal solutions. Although it is still true that the pressure within the membrane and in the vapour phase proper is uniform, the pressure inside the solution is *not* equal to that inside the pure solvent. It is greater or less than the latter according as the heat of dilution of the solution is positive or negative (*cf.* equation [17]).

* *Supra*, p. 436. At osmotic equilibrium the relationship $\partial B = Q$ is absolutely accurate, for the change in internal energy is zero when there is no expansion.

(b) *The Magnitude of the Osmotic Pressure.*

As is well known*, the application of hydrostatic pressure to a solution increases the vapour pressure of the latter, and when a pressure equal to the osmotic pressure is put on the solution, the vapour pressures of the solvent and solution become equal to one another. We may therefore define the osmotic pressure as the hydrostatic pressure which, when applied to the solution, will raise the vapour pressure up to that of the pure solvent, and which incidentally will also bring the pressure generated inside the membrane by the solution up to that generated by the solvent. This definition is, of course, merely a slight extension of the usual definition that the osmotic pressure is the hydrostatic pressure which (when applied to the solution) stops the osmotic flow.

Taking the above definition as the basis, we can now arrive at the magnitude of the osmotic pressure very simply by making use of the relationship between the vapour pressure of a liquid and the hydrostatic pressure to which it is subjected which was first obtained by Sir J. J. Thomson for pure liquids† and extended by A. W. Porter to solutions in general‡.

$$\text{Porter's relationship is } \frac{d\Pi}{dp_1'} = \frac{v}{s}, \dots \dots \dots [18]$$

where Π = hydrostatic pressure.

p_1' = partial vapour pressure of solvent at pressure Π .

v = sp. vol. of vapour at pressure Π .

s = sp. vol. of the solvent in the solution at pressure Π .

(i. e. the loss in vol. when 1 gm. solvent is removed from the solution.)

Multiplying both v and s by the molec. wgt., and assuming that the vapour obeys the simple gas law, we have

$$\frac{d\Pi}{dp_1'} = \frac{RT}{p_1' V_1'}$$

where V_1' is the molec. vol. of the solvent in the solution under the hydrostatic pressure Π , whence

$$d\Pi = \frac{RT}{V_1'} \cdot \frac{dp_1'}{p_1'}$$

* *Supra*, also, p. 439.

† 'Application of Dynamics to Physics and Chemistry,' p. 171.

‡ Proc. Roy. Soc. A. lxxix. p. 519 (1907).

Putting $V_1' = V_{1(a)} - \Pi\beta V_{1'(a)}$, where β is the coefficient of compressibility of the solution and $V_{1'(a)}$ is the mol. vol. of the solvent at the atmos. press., we get

$$d\Pi(1 - \Pi\beta) = \frac{RT}{V_{1'(a)}} \cdot \frac{dp'}{p_1'}.$$

Integrating between the limits represented by the osmotic pressure P and zero hydrostatic pressure*, and remembering that $p_{1'(P)} = p_{1(a)}$, we obtain

$$\int_0^P d\Pi - \beta \int_0^P \Pi d\Pi = \frac{RT}{V_{1'(a)}} \int_{p_{1'(a)}}^{p_{1(a)}} \frac{dp_1'}{p_1'},$$

whence

$$P - \frac{1}{2}\beta P^2 = \frac{RT}{V_{1'(a)}} \log e \frac{p_{1(a)}}{p_{1'(a)}}. \quad [19]$$

This is the general equation connecting the osmotic pressure with the vapour pressure of the pure solvent and solution when both are at the atmospheric pressure. With the exception that V_1' is written for V_1 , it is identical with the equations given by Gibbs, Van Laar, and others. It holds for all solutions irrespective of association of the solvent, formation of solvates, &c., or of abnormalities in latent heat, &c.

Substituting the values of $\frac{p_1}{p_1'}$ given in equation [10], we get for the type of solutions we have been dealing with

$$\begin{aligned} P - \frac{1}{2}\beta P^2 &= \frac{RT}{V_{1'(a)}} \log_e \left\{ \frac{N+n}{N} - \frac{n}{N} \left(1 - \frac{V_2 - b_2 + \epsilon_{(a)}}{V_1 - b_1} \right) \right\} e^{\frac{Q}{RT}}, \\ &= \frac{RT}{V_{1'(a)}} \log_e \left\{ \frac{N+n}{N} - \frac{n}{N} \left(1 - \frac{V_2 - b_2 + \epsilon_{(a)}}{V_1 - b_1} \right) \right\} + \frac{RT}{V_{1'(a)}} \log_e e^{\frac{Q}{RT}}, \\ &= \frac{RT}{V_{1'(a)}} \log_e \left\{ \frac{N+n}{N} - \frac{n}{N} \left(1 - \frac{V_2 - b_2 + \epsilon_{(a)}}{V_1 - b_1} \right) \right\} + \frac{Q}{V_{1'(a)}}. \quad [20] \end{aligned}$$

When the solution is dilute we have $V_1' = V_1$ (see p. 433); the compressibility factor becomes negligible; the expression in brackets becomes equal $\frac{N+n}{N}$ (pp. 433, 434); $\log_e \frac{N+n}{N} = \frac{n}{N}$ approx.; so that the expression reduces to

$$PV_1 = RT \frac{n}{N} + Q \quad [21]$$

* *I. e.* zero mechanical hydrostatic pressure, not counting the atmospheric pressure.

If instead of writing V_1 (*i. e.* the mol. vol. of the liquid solvent) we write V (the volume of solution containing 1 gm. mol. of solute $= \frac{N}{n} V_1$), and q for $\frac{n}{N} Q$, we get

$$PV = RT + q \quad . \quad . \quad . \quad . \quad . \quad [22]$$

This is the simple gas equation corrected for the heat of dilution which has already been given by Bancroft*. In this connexion it is to be noted that the osmotic pressure of a dilute solution is given by the simple gas equation only when the solution has zero heat of dilution. If the heat of dilution is positive the osmotic pressure is abnormally high, whilst if it is negative the osmotic pressure is abnormally low. Bancroft, for instance, has shown that dilute solutions of sulphuric acid in water, sodium in mercury, and resorcinol in alcohol have osmotic pressures which are several times as great as would be given by the gas law; whilst Kahlenberg† has demonstrated that solutions of cane-sugar, lithium chloride, and certain other solutes in pyridine give osmotic pressures which are only a fraction of what the simple gas law would require them to be.

It is apparent also from the method of deriving the preceding equation [22] that the abnormalities in the osmotic pressure of dilute solutions have their origin in abnormalities in the vapour pressure, and hence ultimately in the difference in the intrinsic pressures of the solvent and solution. Traube's surface-tension theory is therefore of value in predicting abnormalities in the osmotic pressure also. As a general rule, if the surface-tension of a solution is low the osmotic pressure would also tend to be low; and *vice versa*. Hence, in many cases, the apparent flow of the solvent from the region of low surface-tension to high (*supra*, p. 440).

(C) Compressibility Relationships at Osmotic Equilibrium.

It has been pointed out previously that the application of hydrostatic pressure to the solution causes both π_1' , p_1' , and ρ_1' to increase, owing to the fact that compression reduces $n\epsilon$ and brings the molecules inside the solution more closely together. We can obtain the contraction at osmotic equilibrium as follows:—

The general equation connecting π_1 and π_1' is [5], viz.

$$\frac{\pi_1}{\pi_1'} = \left\{ \frac{N+n}{N} - \frac{n}{N} \left(1 - \frac{V_2 - b_2 + \epsilon}{V_1 - b_1} \right) \right\}.$$

* Journ. Phys. Chem. x. p. 322 (1906).

† *Ibid.* x. p. 141 (1906).

But at osmotic equilibrium,

$$\frac{\pi_1}{\pi_1'} = e^{-\frac{Q}{RT}} = 1 - \frac{Q}{RT}$$

(see p. 443).

Hence, if $\epsilon_{(P)}$ is the total expansion per solute molecule when the solution is under the hydrostatic pressure P^* (*i. e.* the osmotic pressure), we have

$$\frac{N+n}{N} - \frac{n}{N} \left(1 - \frac{V_2 - b_2 + \epsilon_{(P)}}{V_1 - b_1} \right) = 1 - \frac{Q}{RT};$$

whence

$$n\epsilon_{(P)} = -n(V_2 - b_2) - \frac{N(V_1 - b_1)Q}{RT}. \quad [23]$$

Now the contraction due to applying the osmotic pressure to the solution is $n\epsilon_{(a)} - n\epsilon_{(P)}$; and if β is the average coefficient of compressibility of the solution† between zero pressure and the osmotic pressure, it is also equal to $P\beta(NV_1' + nV_2')$.

Hence

$$P\beta(NV_1' + nV_2') = n\epsilon_{(a)} - n\epsilon_{(P)}, \quad [24]$$

where $\epsilon_{(a)}$ and $\epsilon_{(P)}$ have the values given to them by equations [7] and [23] respectively.

For dilute solutions with no heat of dilution, we can neglect nV_2' ; and substituting the values of $\epsilon_{(a)}$ and $\epsilon_{(P)}$ for such solutions, the equation becomes

$$P\beta NV_1 = n\{(V_1 - b_1) - (V_2 - b_2)\} - \{-n(V_2 - b_2)\} \\ = n(V_1 - b_1).$$

Putting

$$PV_1 = RT \frac{n}{N},$$

this becomes

$$RT \frac{n}{N} \cdot N\beta = n(V_1 - b_1);$$

whence

$$\beta = \frac{V_1 - b_1}{RT}$$

$$\text{and } V_1 - b_1 = \beta RT \dagger, \quad [25]$$

* *Supra*, p. 432. The value of ϵ varies with the hydrostatic pressure placed on the solution, diminishing with increase of the latter and tending to become more and more negative with high pressures.

† Defined as the shrinkage of 1 c.c. per atmosphere applied.

‡ It is to be remembered that, since P is measured in atmospheres and V in c.c., the constant R is measured in c.c. atmospheres and is equal to 82.07.

or in words, the free space within a dilute solution having no heat of dilution is equal to RT times the coefficient of compressibility. This relationship is important, for it enables the "free space" within a dilute solution to be calculated very easily. Since the pure solvent is the limiting case of a dilute solution, and has perforce no heat of dilution, it will be seen that the above relationship should hold absolutely for pure liquids. It is to be noted, however, that the coefficient of compressibility must be taken at atmospheric pressure and not at relatively high pressures*.

We can now use equation [25] for obtaining the general equation for the osmotic pressure in terms of the concentrations, volume change on solution, and the coefficients of compressibility β_1 , β_2 , and β for the pure solvent, pure solute, and solution respectively.

From equation [20], viz.

$$PV_1'_{(a)} \left(1 - \frac{1}{2} \beta P\right) = RT \log_e \left\{ \frac{N+n}{N} - \frac{n}{N} \left(1 - \frac{V_2 - b_2 + \epsilon_{(a)}}{V_1 - b_1}\right) \right\} + Q,$$

by substituting

$$(V_1 - b_1) = \beta_1 RT, \quad V_2 - b_2 = \beta_2 RT,$$

$$\text{and } V_1'_{(a)} = V_{1(a)} - \frac{n}{N+n} \{(V_1 - b_1) - (V_2 - b_2 + \epsilon_a)\}$$

(cf. equation [7]),

we get

$$P \left\{ V_{1(a)} - \frac{nRT}{N+n} \left(\beta_1 - \beta_2 - \frac{\epsilon}{RT} \right) \right\} \left\{ 1 - \frac{1}{2} \beta P \right\} = RT \log_e \left\{ \frac{N+n}{N} - \frac{n}{N} \left(\frac{\beta_1 - \beta_2 + \frac{\epsilon_{(a)}}{RT}}{\beta_1} \right) \right\} + Q.$$

β_1 and β_2 are both usually very small, so that we can count $\beta_1 - \beta_2$ as zero without appreciable error.

The equation then becomes

$$P \left(V_1 + \frac{n\epsilon_{(a)}}{N+n} \right) \left(1 - \frac{1}{2} \beta P \right) = RT \log_e \left\{ \frac{N+n}{N} - \frac{n\epsilon_{(a)}}{N\beta_1 RT} \right\} + Q. \quad [26]$$

It is clear also that with all but the strongest solutions we

* As is well known, the coefficient of compressibility varies considerably with the pressure.

can neglect $\frac{n\epsilon_{(a)}}{N+n}$, $\frac{n\epsilon_{(a)}}{N\beta_1 RT}$, and also $\frac{1}{2}\beta P$; so that we have, for most moderately strong solutions,

$$PV_1 = RT \log_e \frac{N+n}{N} + Q. \quad . \quad . \quad . \quad [27]$$

This equation is similar to that Van Laar and others have given for the ideal solution, except that the heat of dilution is included.

Apart from the fact that the method of analysis adopted in the preceding pages throws much light on the anomalies of osmotic pressure and osmotic flow, still further confirmation of its intrinsic soundness becomes apparent when we consider in detail the fundamental relationship which has been deduced between the coefficient of compressibility of a liquid and its free space.

The following table shows the value of $(V-b)$ for various liquids, calculated from equation [20] by means of compressibility data given in Landolt-Bornstein. The value of the pressure inside the liquid is also given, being calculated from the relationship $\pi\beta=1$ *.

| Liquid. | Temp. °C. | Compressibility, $\beta \times 10^6$. | $(V-b)$, in c.c. | π , in atmos. |
|-------------------|--------------|---|----------------------|----------------------|
| Ether | 13.5 | 169 (at from 8-25 atmos.) | 3.97 | 5920 |
| Ethyl Chloride... | 15.2 | 153 „ 8-34 „ | 3.60 | 6550 |
| Ethylene | 10.0 | 68 — | 1.58 | 14700 |
| Ethyl Acetate ... | 13.3 | 104 „ 8-37 „ | 2.44 | 9600 |
| Benzene | 16.0 | 90 „ 8-37 „ | 2.13 | 11100 |
| Amylene..... | 13.0 | 172 „ 8-37 „ | 4.05 | 5810 |
| Pentane | 20.0 | 318 — | 7.63 | 3150 |
| Hexane | 23.0 | 159 „ 0-1 „ | 3.85 | 6290 |
| Heptane..... | 23.0 | 134 „ 0-1 „ | 3.25 | 7460 |
| Octane | 23.0 | 121 „ 0-1 „ | 2.94 | 8270 |

The subjoined table gives the figures for ethyl ether at various temperatures also, Amagat's compressibility data being used †.

The intrinsic pressures calculated from the relationship in question are evidently of the usually accepted order of

* This simple relationship follows immediately from the two relations $\beta = \frac{V-b}{RT}$ and $\pi = \frac{RT}{V-b}$.

† *Ann. Chim. Phys.* (6) xxix. p. 505 (1893).

| Temp. ° C. | Compressibility, $\beta \times 10^6$, at from 50-100 atmos. | (V-b), in c.c. | π , in atmos. |
|---------------|--|-------------------|----------------------|
| 0 | 133 | 2.98 | 7520 |
| 20 | 158 | 3.79 | 6400 |
| 40 | 203 | 5.25 | 4940 |
| 60 | 252 | 6.89 | 3970 |
| 80 | 315 | 9.13 | 3180 |
| 100 | 395 | 12.00 | 2540 |

magnitude of a few thousand atmospheres; whilst, as should also be the case, the values for the free space are relatively small as compared with the volumes of the molecules themselves.

*XLII. Studies of the Ultra-violet Transparency of Certain Coloured Media. By H. W. L. ABSALOM, B.Sc., A.R.C.S.**

THE present investigation originated in an attempt to find some colouring matter which, while opaque in the yellow region of the spectrum, should transmit as far as possible into the ultra-violet. Such a material would be of great use in developing certain investigations on the fluorescence of sodium vapour which have been made in this laboratory (see Strutt, Proc. Roy. Soc. Nov. 1915).

With this object a number of little-known colouring matters were examined, and the subject was afterwards pursued for points of interest it was found to possess in itself.

The coloured metallic salts and the aniline dyes have already been well explored (see Uhler and Wood, 'Atlas of Absorption Spectra'), but few of them possess much ultra-violet transparency. Attention was turned therefore to the blue rock-salt of Stassfurt, believed to owe its colour to colloidal sodium. This was found to be very transparent, and the observation led on to investigation of other naturally coloured minerals and precious stones as well as to various preparations of colloidal metals, such as the solutions of alkali metals in anhydrous liquid ammonia.

I. Gems and Minerals.

The arc between copper poles was employed as the source of radiation. By means of a small quartz spectrograph, photographs were obtained of the portion of the spectrum between $\lambda 5000$ and $\lambda 2250$. The specimen under exami-

* Communicated by the Author.

nation was fixed with wax over a small hole in a screen of sheet ebonite, in such a way that no radiation could reach the slit of the spectrograph save after transmission through the specimen. In the case of a cut stone care was taken that it was orientated so that the light had the best chance of transmission, and in minerals where the distribution of colour was irregular the convergent radiation was in general directed so as to traverse the part of deepest colour. Several exposures of varying duration were made with each specimen, the maxima ranging from ten to thirty minutes according to the nature of the specimen.

In the following table the wave-lengths denote the point at which complete absorption commences.

| | λ |
|--|-------------|
| 1. Natural blue rock-salt..... | Beyond 2250 |
| 2. Natural rock-salt coloured by cathode rays.. | Beyond 2250 |
| 3. Sylvite, white | Beyond 2250 |
| 4. Ditto, coloured blue by cathode rays | Beyond 2250 |
| 5. Chili saltpetre, ordinary white variety | 3512 |
| 6. Ditto, violet | 3248 |
| 7. Fluorspar, coloured deep violet by cathode rays | Beyond 2250 |
| 8. Diamond, yellow | 3200 |
| 9. Ditto, blue | 3150 |
| 10. Kunzite | 3050 |
| 11. Garnet, red | 4023 |
| 12. Zircon (hyacinth) red-brown | 2618 |
| 13. Ditto, decolorized by heat..... | 2442 |
| 14. Ditto, green..... | 4023 |
| 15. Ditto, yellow | 4023 |
| 16. Topaz, pale yellow.. .. | 2618 |
| 17. Ditto, dark yellow..... | 2294 |
| 18. Ditto, pale pink-brown | 2618 |
| 19. Ditto, blue | 2961 |
| 20. Emerald | 3200 |
| 21. Ruby | 3000 |
| 22. Tourmaline, green | 3512 |
| 23. Ditto, green-yellow | 3000 |
| 24. Ditto, pink | 3064 |
| 25. Spinel, blue | 4023 |
| 26. Ditto, purple | 3248 |
| 27. Ditto, pink | 3000 |
| 28. Kyanite, blue | 3200 |
| 29. Beryl, blue | 3274 |
| 30. Cordierite, blue-purple | 3248 |
| 31. Cairngorm | 3248 |

Notes on the above:—

1. This is the natural blue rock-salt of Stassfurt. It is said to be found at the boundary of the salt with some of the potash minerals.

2. Ordinary white rock-salt coloured a deep blue by cathode-ray bombardment. This has always been considered kindred to the natural blue salt, and is now seen to behave

like it in this respect also. The colour is, however, superficial instead of being diffused through the mass.

6. This pale violet variety of Chili saltpetre, occurring naturally, can be decolorized by heat, like the blue rock-salt. The colour may then be restored by cathode-ray bombardment. The same colour can be in some measure imparted to a piece of the ordinary white Chili saltpetre by bombardment, but in this case the coloration is not uniform but banded, suggesting that its development depends on some impurity.

7. The specimen was originally greenish in colour, but the violet colour imparted by bombardment was very much deeper.

II. *Solutions of Metals in Liquid Ammonia.*

It has been known for some years that the metals sodium, potassium, lithium, rubidium, caesium, barium, strontium (and magnesium to a less extent), react with liquid ammonia, producing fine blue colorations. The blue colour is not permanent; its duration varies with the metal and with the purity and dryness of the metal and the ammonia. It is believed that the metal dissolves in the ammonia forming the blue colloidal solution, and that then a reaction occurs resulting in the formation of an amide with the liberation of hydrogen—the disappearance of the colour marking the final conversion of the metal in solution into amide. The stability of solutions increases in the order potassium, calcium, lithium, sodium. Considerable attention has been devoted to the reaction which takes place and to the physico-chemical properties of the solutions. (Moissan, *Comptes Rendus*, 1898; Krauss, *J. Am. Chem. Soc.* 1907, 1908, 1914.)

Recently Argo and Gibson (*Phys. Rev.* Feb. 1916) have studied the absorption of the blue solutions of sodium, potassium, and magnesium by means of the spectro-photometer. There appears to be no record of observations carried out in the ultra-violet region.

In the present instance attempts were made initially to obtain the blue solutions of sodium in liquid ammonia. Some .880 solution of liquid ammonia was heated and the gaseous ammonia led through a long tube packed with soda-lime, and thence by a very thin drawn-out tube into a silica tube surrounded by a freezing-mixture of solid carbon dioxide and methylated spirits. When sufficient liquid ammonia had collected, a small piece of sodium, as free as possible from oxide and moisture, was introduced and the silica tube then sealed off. As soon as the tube was removed from the freezing-mixture the metal seemed to swell somewhat, and the contents of the tube soon assumed a deep blue clotted appearance. Similar results were obtained with potassium

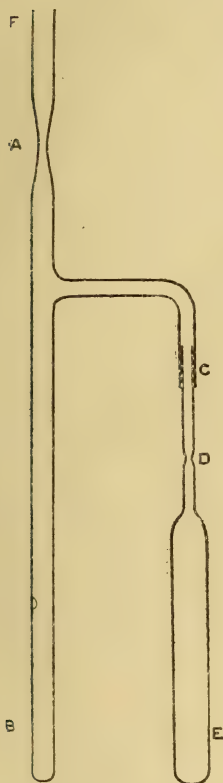
and calcium. In all cases the colour persisted but for a few days, and sometimes disappeared very rapidly if only a small piece of the metal had been used. A white precipitate remained. The almost opaque nature of the contents of the tube rendered the photography of absorption spectra difficult. By supporting the tube horizontally and rotating steadily it was hoped to obtain a sufficiently transparent and uniform film, but the liquid did not adhere sufficiently well to the walls of the tube. Ultimately attempts to obtain photographs were made as the blue colour became less dense. The tube was fitted tightly into a deep cork. A hole at right angles to the former allowed light to traverse the liquid. The results with a calcium solution were the most satisfactory, but even these were not altogether consistent.

More recently solutions of magnesium have been obtained by Cottrell (J. Phys. Chem. 1914.) He found that with freshly scraped metal and dry ammonia blue solutions resulted which were of considerable permanence, persisting in one case for several years.

The apparatus in the present case is shown.

CE was of silica, the remainder of glass. A few small pieces of freshly scraped magnesium ribbon were introduced into E, which had been previously cleaned and dried. A constriction was made at D and the silica tube then joined to the glass by means of a sealing-wax joint at C. F was connected to a Gaëde pump, and when the pressure was very low E was heated

to disengage any gases. (Cottrell, *ibid.*) The pump was then disconnected, B immersed in liquid air and ammonia collected as a solid in the way described above. A few pieces of sodium were dropped into B to account for any water which may have passed over with the ammonia. The pump was again connected and the tube sealed off at A. B was removed from the liquid air, and when the ammonia had liquefied E was immersed in the liquid air and the ammonia distilled over. The liquid contents of E were afterwards washed back into B, and then distilled over to E again. The silica was sealed off



at D. The blue colour appeared within a few hours, and with one solution has lasted to the time of writing—nearly three months.

A piece of black paper was wrapped round the tube and pasted along a narrow strip. In it were made two small holes diametrically opposite. The diameter of the tube was 1.5–2 cm., so that the light was incident practically normally at one hole, and it was impossible for light from the arc to reach the spectrograph without having traversed the solution.

Exposures varying from 10–600 seconds were made with both pale and deep blue solutions, and in all cases total absorption commenced at $\lambda 2442$. The limit of transmission for liquid ammonia is $\lambda 2393$. (In the earlier experiments with calcium absorption seemed to commence at $\lambda 2618$.)

Hence the blue solutions transmit for a considerable distance into the ultra-violet, but they could not be used for screening purposes in flat-sided cells on account of the high vapour-pressure of ammonia at ordinary temperatures. Solutions in the primary amines which have higher boiling-points would be more suitable.

Lithium and caesium dissolve in methyl-amine (boiling-point -6° C.), lithium dissolves in ethyl-amine (19° C.). (Moissan, *Comptes Rendus*, 1899; Rengade, *ibid.* 1905.) Solutions in the higher primary amines have not been obtained.

Attempts to prepare solutions of lithium and magnesium in ethyl-amine by the above method proved unsuccessful, probably because the ethyl-amine was not properly dry.

Experiments have also been made on a solution of colloidal gold (after Faraday). When freshly prepared the limit of transmission was $\lambda 2492$. After a day had elapsed it had moved to $\lambda 2767$.

Discussion of Results.

One general result is that transparency far into the ultra-violet is much more commonly met with in the case of colour due to colloidal metals than it has been found to be in ordinary coloured salts or aniline dyes. This is clearly illustrated by the natural blue rock-salt and the various salts and minerals coloured by cathode rays. We cannot, of course, expect to find ultra-violet transparency in the coloured substance unless it was present before coloration. Thus the violet Chili saltpetre is opaque in the ultra-violet light, but this opacity is equally met with in white samples: on the other hand, where the uncoloured substance is transparent, coloration in the visible region by bombardment leaves this unaffected.

The nature of the colouring matter in gems is in many cases

undetermined, nothing appearing in the analyses to account for it. It was thought that colloidal metals might in some cases be concerned; and if ultra-violet transparency were found, this would be considerable evidence for such a view. It has been found that the variety of zircon called hyacinth only begins to be opaque at $\lambda 2617$, and one variety of yellow topaz at $\lambda 2294$. In these cases the presumption is strong that the colouring matter is of the nature of a colloidal metal.

The extreme ultra-violet transparency of the solution of magnesium in ammonia confirms the view that these metallic solutions are to be regarded as colloidal.

The author desires to acknowledge his gratitude to Professor the Hon. R. J. Strutt, F.R.S., for suggesting the work, and for continuous interest and advice.

Physics Department,
Imperial College of Science and
Technology, S.W.

XLIII. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 296.]

January 24th, 1917.—Dr. Alfred Harker, F.R.S., President,
in the Chair.

Mr. SCORESBY ROUTLEDGE, M.A., gave an account of Easter Island. He said that the Expedition, that he had had the honour to command, was organized with the object of carrying out a long-standing wish of various bodies interested in anthropology. This wish was that Easter Island, and other islands most near to it, though far distant from it, should be thoroughly examined, and that all information and material thereon found should be carefully considered on the spot, or, if possible, be brought back for comparative study.

This programme necessitated a vessel being specially designed, built, and equipped for the purpose. A schooner with auxiliary motor power, the 'Mana,' of 90 tons gross register, 78 feet on the water-line, 20 feet beam, and drawing 10.5 feet aft, was accordingly completed by the end of 1912, and she sailed from Southampton in February 1913 with a company of twelve all told, of whom four formed the scientific staff. After the longest voyage ever made by a yacht under canvas, she sailed into Southampton again in June 1916, without having experienced accident to man or material.

The course taken was through the Magellan Straits, and thence through the labyrinth of Andean waterways that stretch north therefrom, and are known as the Patagonian Channels.

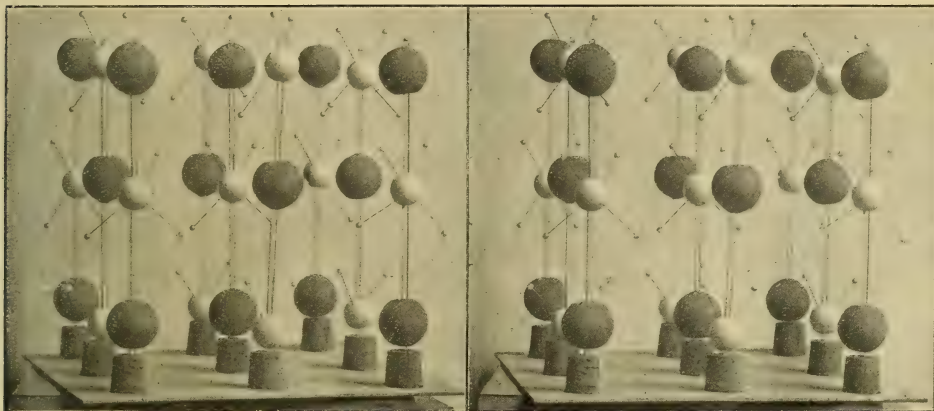
On reaching Juan Fernandez Island, the 'Mana' had to put back to Valparaiso because the geologist of the Expedition, the late Mr. F. L. Corry, had contracted typhoid fever on the Chilean coast. Mr. Corry never recovered sufficiently to allow him to

rejoin the Expedition. Hence no formal geological report on the island could be submitted to the Meeting. It was thought best, therefore, to endeavour to convey the conditions existent on Easter Island by means of a series of panoramic and other photographs, specially taken to illustrate geological features. As these very largely consist of coast-sections, the opportunity was taken to show, and explain, other pictures that were closely associated with them. Such were the ruins of the village called Orongo, consisting of peculiar canoe-shaped houses built of imbricated slabs of shale, with the roof convex, both longitudinally and transversely, on its exterior aspect, and covered with earth. They are romantically situated on the rim of the volcano of Rano Kao, with an almost sheer drop of 900 feet into the sea, or of 600 feet into the crater-lake. At Orongo, too, are found certain large rocks, carved with the symbol of a bird-headed man, holding in its hand an egg. A cult, based on annually obtaining the first-laid egg of a certain migratory sea-bird, was thus gradually brought to light, and appears to be a unique form. A brief outline only could be given of some of the knowledge obtained concerning the peculiar routine associated with seeking, and taking, the sacred egg, and of the part which it occupied in the former religious life of the island.

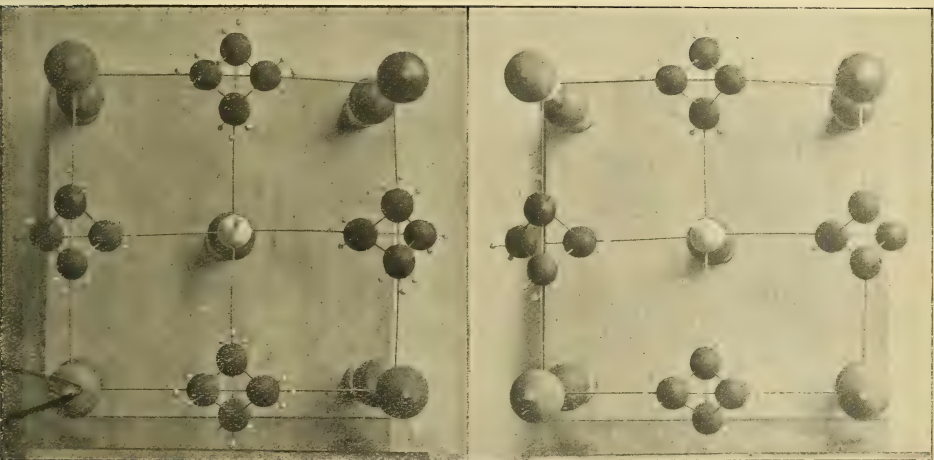
Proceeding along the coast, typical examples of the great terraces, and their giant stone figures, were shown, and their leading characteristics discussed. A submarine freshwater spring, near the great image-terrace of Tongariki, and opposite certain typical lava-formed caves, gave occasion to the lecturer to explain how had arisen the longstanding, and world-wide spread report, that man and beast on Easter Island habitually drink sea-water, in the place of fresh.

The old volcano of Rano Raraku, the centre of the former religious life of the island, was then described. A series of panoramic pictures, preceded by an accurate survey made by Lieut. R. D. Ritchie, R.N., the Cartographer of the Expedition, showed a crater-lake surrounded by a rim of tuff which rises to a height of 540 feet above the surrounding plain. The plain is undulating in surface, formed superficially of hard, dense, but nevertheless vesicular, lava, and it rests on compact non-columnar basalt. One section of this crater wall, some 600 yards long, on both its interior and exterior aspects, was seen to be quarried right up to the highest point. On the mountain-face, both inside and out, large numbers of statues, in every state of completion, were to be seen. The largest of these measured 68 feet in length. Some of those excavated by the Expedition exhibited fine details, such as the finger-nails, in perfect condition.

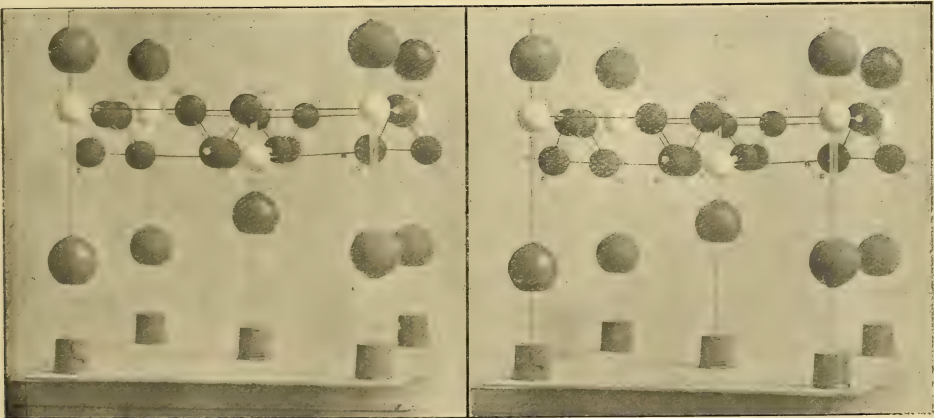
In conclusion, Easter Island might be described as a plateau of basalt raised from 50 to 100 feet above the sea. Superimposed on this were numerous cones ranging up to nearly 2000 feet. The plateau was covered but sparsely with soil, and could only be crossed with difficulty in any direct line. The cones, on the other hand, were generally smooth of surface, with a good depth of soil. Nevertheless the island is practically without trees, bushes, or shrubs.



a



b



THE
LONDON, EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

[SIXTH SERIES.]

JUNE 1917.



XLIV. *The Motion of a Particle on the Surface of a Smooth Rotating Globe.* By F. J. W. WHIPPLE*.

1. **T**HE problem which is discussed in the following notes has not received the consideration which its physical interest merits. There is no reference to it in the standard text-books on Dynamics.

Sprung considered it from the meteorologist's point of view in a paper published in Wiedemann's *Annalen*, vol. xiv. 1881, and now accessible to English readers in Cleveland Abbe's 'Third Collection of Papers on the Mechanics of the Earth's Atmosphere,' but he does not go into detail in the analysis of the various cases which can arise. He confines his attention to motion near the poles, and with reference to the wider problem he writes: "the solution of this problem leading to elliptic integrals does not seem to be worth while . . . since the notion formerly entertained, that the particles of air actually follow the 'inertia path' has been completely refuted by synoptic weather-charts." The contrary view that the nature of the forces which produce the actual paths will be realized more readily and more fully if the "inertia paths" are known seems to be more consistent with general experience. The study of motion under no forces should precede the theoretical study of motion governed by pressure.

* Communicated by the Director of the Meteorological Office.
Phil. Mag. S. 6. Vol. 33. No. 198. June 1917. 2 K

2. For many purposes the departure of the earth from a spherical form can be neglected, and it is therefore interesting to approach our problem by considering, in the first instance, the motion of a particle on the surface of a smooth rotating sphere. The reaction between the particle and the sphere is in this case radial and so is the gravitational force. Accordingly, the motion of the particle in space is the same as it would be if the globe did not revolve. The path relative to the centre of the sphere is accordingly a great circle. To fix our ideas we take a particle starting at relative rest in latitude λ . Its velocity in space is $R\omega \cos \lambda$, where R is the radius and ω the angular velocity of the sphere. The time of revolution of the particle in its orbit is $2\pi R/(R\omega \cos \lambda)$ or $T \sec \lambda$, where T is the period of the rotation of the sphere. Let us suppose that the particle starts from a point in the northern hemisphere. The track on the sphere leads southward to begin with. To find the angle at which it crosses the equator we notice that the relative velocity at the crossing is compounded of $R\omega \cos \lambda$, making the angle λ with the equator and of $R\omega$ along the equator. The relative velocity is therefore $R\omega \sin \lambda$, in a direction making an angle λ with the meridian. The particle approaches the equator from the north-east.

At the most northerly and southerly points of the track there are cusps. The difference of longitude between consecutive cusps on either side of the equator is $(\omega T \sec \lambda - 2\pi)$ or $(\sec \lambda - 1)2\pi$. If the range of latitude is small, this angle is approximately $\lambda^2\pi$.

The track can be specified in polar coordinates. Let λ, ϕ' be coordinates relative to axes fixed in space, λ being the latitude and ϕ' the longitude reckoned towards the east from a meridian which does not turn with the globe and which passes through the initial position of the particle. The coordinates of this position are $\lambda_0, 0$.

The angular distance moved by the particle is $\omega t \cos \lambda_0$, and we have the equations

$$\sin \lambda = \sin \lambda_0 \cos (\omega t \cos \lambda_0),$$

$$\cos \phi' = \cot \lambda_0 \tan \lambda.$$

Let ϕ be the longitude reckoned towards the west from the meridian turning with the globe and passing through the initial position of the particle, then

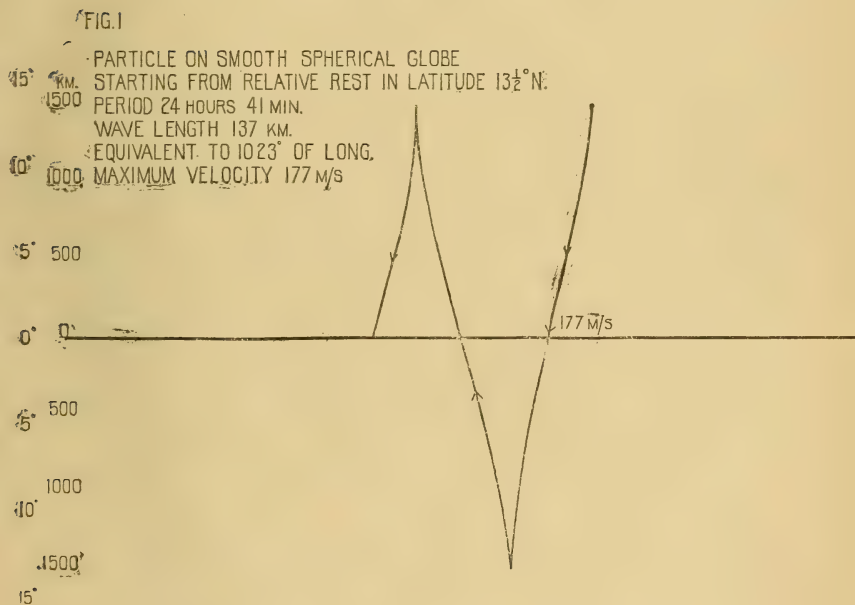
$$\phi + \phi' = \omega t.$$

Hence the λ, ϕ equation of the track is

$$\phi = \sec \lambda_0 \cos^{-1} \left(\frac{\sin \lambda}{\sin \lambda_0} \right) - \cos^{-1} \left(\frac{\tan \lambda}{\tan \lambda_0} \right).$$

Other tracks on the rotating sphere corresponding with other initial conditions will have similar features, though the cusps will not usually occur. In every case the track crosses the equator, and the velocity of the particle relative to the sphere reaches a value of the same order of magnitude as the velocity with which the surface of the sphere is moving itself*.

Fig. 1.



3. Turning to the problem of the motion of a particle on a smooth rotating globe bounded by a "level" surface, we notice in the first place that every point on the globe is a position of equilibrium. As the particle moves on the surface the relative velocity V remains constant. Owing to the rotation of the globe, the track of the particle is curved.

* The diagram (fig. 1) illustrates motion on a sphere with circumference 40,000 km. rotating once in 24 hours.

It can be shown that ρ , the geodesic radius of curvature, is given * by the equation

$$V^2/\rho = 2\omega V \sin \lambda, \quad . \quad . \quad . \quad . \quad . \quad (3.1)$$

or

$$\rho = \frac{V}{2\omega \sin \lambda}. \quad . \quad . \quad . \quad . \quad . \quad (3.2)$$

The curvature is to the right in the northern hemisphere, to the left in the southern. The equation indicates that if the velocity is small, so that variation in latitude is negligible, the track is a circle which is described in the anti-cyclonic sense, *i. e.* clockwise in the northern hemisphere, anti-clockwise in the southern.

The time of one revolution is $2\pi/2\omega \sin \lambda$ or $\frac{1}{2} \operatorname{cosec} \lambda$ days, the length of one (sidereal) day being $2\pi/\omega$.

At the poles the period is $\frac{1}{2}$ day, in latitude 60° it is $\cdot 58$ day, and in latitude 30° it is one day.

4. The case of motion in the neighbourhood of the pole is of special interest.

If the pole is the centre of the circle, then the velocity of the particle relative to the earth being $2\omega\rho$ the velocity in space is $\omega\rho$, *i. e.* the particle moves with the same speed as the ground over which it is travelling but in the opposite direction. The horizontal component of gravity, being sufficient to maintain in relative equilibrium a particle resting on the surface, is also sufficient to maintain in circular motion a particle moving with the same speed in the opposite direction. Evidently two such particles pass one another twice in the course of a day, so that the statement that the period of the relative motion is half a day is verified.

If the track of the moving particle crosses the pole, the motion in space is simple harmonic. The acceleration due to the horizontal component of gravity is $\omega^2 r$ at a distance r from the pole, and the period of this motion is one day. The same point of the surface of the globe is, however, under the particle at each end of its swing, so that the period of the relative motion is again seen to be half a day.

5. In low latitudes the assumption that the variation in λ may be neglected is not legitimate. In such latitudes a good approximation to the path may be found by writing λ for $\sin \lambda$, so that $\rho = V/2\omega\lambda$. If we think of a belt near the equator as developed into a plane, $R\lambda$ is the ordinate of a

* Various proofs of this formula have been given. Three of them will be found in the 'Computer's Handbook' of the Meteorological Office.

point on the track and the curvature of the track is proportional to the ordinate. The track is therefore an elastica, the curve made by a thin rod strained by forces applied at the two ends. The various forms which the elastica can take were classified by Euler. An account of these is to be found in Love's 'Theory of Elasticity,' vol. ii. The most detailed study of the subject is that of Hess (*Math. Ann.* 1885).

As we wish to obtain numerical results, it is desirable to work out our problem without assuming a knowledge of the elastica.

6. Let u, v be the components of velocity towards the east and towards the north respectively. As the velocity relative to the earth is a constant V ,

$$u^2 + v^2 = V^2. \quad . \quad . \quad . \quad . \quad . \quad (6.1)$$

The forces acting on the particle are in the meridian and therefore they have no moment about the axis of the globe. Accordingly, by the Conservation of Angular Momentum, we can write down the equation

$$R' \cos \lambda [u + R' \omega \cos \lambda] = \text{constant}, \quad . \quad . \quad (6.2)$$

where R' is the length of the normal terminated by the polar axis.

If ωM be written for the constant angular momentum

$$u = \omega \left[\frac{M - R'^2 \cos^2 \lambda}{R' \cos \lambda} \right], \quad . \quad . \quad . \quad (6.21)$$

whence

$$u = \omega \left[\frac{R'^2 \sin^2 \lambda - (R'^2 - M)}{R' \cos \lambda} \right]. \quad . \quad . \quad (6.22)$$

This equation holds good in the general case, whatever the latitude may be. When λ is small throughout the motion $1 - M/R'^2$ is also small, and it follows that we may use the approximation

$$u = R\omega [\lambda^2 - (1 - M/R^2)], \quad . \quad . \quad . \quad (6.23)$$

where R is the equatorial radius.

The velocity in the meridian is given by

$$v = R \frac{d\lambda}{dt}. \quad . \quad . \quad . \quad . \quad . \quad (6.3)$$

Hence

$$\begin{aligned} R^2 \left(\frac{d\lambda}{dt} \right)^2 &= v^2 = V^2 - u^2 \\ &= V^2 - R^2 \omega^2 [\lambda^2 - (1 - M/R^2)]^2 \\ &= R^2 \omega^2 [\lambda_0^2 - \lambda^2] [\lambda^2 + C], \quad \dots \quad (6.4) \end{aligned}$$

where C is a constant, which may be positive or negative, and λ_0 is the latitude in which the particle is moving to the east.

Thus
$$\frac{d\lambda}{dt} = \pm \omega [(\lambda_0^2 - \lambda^2)(\lambda^2 + C)]^{1/2}. \quad \dots \quad (6.41)$$

Three cases have to be considered, as C may take either sign or vanish.

7. Case I.— C positive.

Let $C = \lambda_0^2 \mu^2$, so that

$$\omega dt = - \frac{d\lambda}{[(\lambda_0^2 - \lambda^2)(\lambda^2 + \mu^2 \lambda_0^2)]^{1/2}} \dots \quad (7.1)$$

The northerly component of the velocity vanishes only in latitude λ_0 North or South, so that the track must cross and recross the equator. The negative sign is introduced as, if the time is measured from the instant at which $\lambda = \lambda_0$, λ will be decreasing to begin with.

To effect the integration, elliptic functions must be used.

We write

$$\lambda = \lambda_0 \operatorname{cn} \psi \quad \dots \quad (7.21)$$

$$(\lambda_0^2 - \lambda^2)^{1/2} = \lambda_0 \operatorname{sn} \psi \quad \dots \quad (7.22)$$

$$(\mu^2 \lambda_0^2 + \lambda^2)^{1/2} = (\mu^2 + 1)^{1/2} \lambda_0 \operatorname{dn} \psi, \quad \dots \quad (7.23)$$

so that the modulus k is given by

$$k^2 = (\mu^2 + 1)^{-1}, \quad \dots \quad (7.24)$$

and the differential equation is satisfied if

$$\psi = \lambda_0 (\mu^2 + 1)^{1/2} \omega t. \quad \dots \quad (7.25)$$

Comparison with equations (6.4), (6.23) shows that

$$V = \frac{1}{2} R \omega (\mu^2 + 1) \lambda_0^2 \quad \dots \quad (7.26)$$

and
$$u = R \omega [\lambda^2 + \frac{1}{2} (\mu^2 - 1) \lambda_0^2] \quad \dots \quad (7.27)$$

$$= R \omega \lambda_0^2 (\mu^2 + 1) [\operatorname{dn}^2 \psi - \frac{1}{2}]. \quad \dots \quad (7.28)$$

The longitude ϕ can be found from the equation

$$R \frac{d\phi}{dt} = u. \quad \dots \quad (7.3)$$

If ϕ be reckoned from the meridian crossed at $t=0$

$$\phi = \lambda_0 (\mu^2 + 1)^{1/2} \int_0^\psi (\operatorname{dn}^2 \psi - \tfrac{1}{2}) d\psi. \quad (7.31)$$

The longitude ϕ_A of the point A, where the path crosses the equator for the first time, is given by writing $\psi = K$, where K is the quarter period of the elliptic function, and, therefore,

$$\phi_A = \lambda_0 (\mu^2 + 1)^{1/2} (E - \tfrac{1}{2}K), \quad (7.32)$$

where, as is usual, $E = \int_0^K \operatorname{dn}^2 \psi d\psi$.

Tables of the function $\operatorname{zn} \psi$ defined by

$$\operatorname{zn} \psi = \int_0^\psi (\operatorname{dn}^2 \psi - E/K) d\psi$$

have been published.

In this notation

$$\phi = \lambda_0 (\mu^2 + 1)^{1/2} \left[\operatorname{zn} \psi + \left(\frac{E}{K} - \frac{1}{2} \right) \psi \right]. \quad (7.33)$$

The angle α at which the track crosses the equator is given by

$$\cos \alpha = \frac{u}{V} = \frac{\mu^2 - 1}{\mu^2 + 1}, \quad (7.4)$$

so that

$$\cot \frac{\alpha}{2} = \mu \quad \text{and} \quad \sin \frac{\alpha}{2} = k. \quad (7.41)$$

If the track is regarded as determined by V and α , then λ_0 may be found from equation (7.26), which takes the form

$$\lambda_0 = \sqrt{\frac{2V}{R\omega}} \sin \frac{\alpha}{2}. \quad (7.5)$$

From (7.25), (7.26) it follows that the periodic time is

$$\frac{2K}{\pi} \sqrt{\frac{R\omega}{2V}} \text{ days}. \quad (7.6)$$

The different subcases which occur as α is given different values will be considered when we come to numerical examples.

8. Case II.— $C=0$.

In this case

$$\omega dt = - \frac{d\lambda}{\lambda(\lambda_0^2 - \lambda^2)^{1/2}}. \quad (8.1)$$

The elliptic functions degenerate into hyperbolic functions, and the solution is given by

$$\lambda = \lambda_0 \operatorname{sech} \psi \quad . \quad . \quad . \quad . \quad . \quad . \quad (8.21)$$

and
$$\phi = \lambda_0 [\tanh \psi - \tfrac{1}{2} \psi], \quad . \quad . \quad . \quad . \quad (8.22)$$

where
$$\psi = \lambda_0 \omega t. \quad . \quad . \quad . \quad . \quad . \quad . \quad (8.23)$$

For large values of t , λ tends to zero, so that the track approaches the equator asymptotically.

9. Case III.— C negative.

Let $C = -\lambda_0^2 \mu^2$, so that

$$\omega dt = - \frac{d\lambda}{[(\lambda_0^2 - \lambda^2)(\lambda^2 - \lambda_0^2 \mu^2)]^{1/2}}. \quad . \quad . \quad (9.1)$$

The northerly component of the velocity vanishes for $\lambda = \lambda_0$ and also for $\lambda = \lambda_0 \mu$, so that the path consists of loops on one side of the equator.

The integration is effected by taking

$$\lambda = \lambda_0 \operatorname{dn} \psi \quad . \quad . \quad . \quad . \quad . \quad . \quad (9.21)$$

$$(\lambda_0^2 - \lambda^2)^{1/2} = (1 - \mu^2)^{1/2} \lambda_0 \operatorname{sn} \psi \quad . \quad . \quad . \quad (9.22)$$

$$(\lambda^2 - \lambda_0^2 \mu^2)^{1/2} = (1 - \mu^2)^{1/2} \lambda_0 \operatorname{cn} \psi. \quad . \quad . \quad (9.23)$$

The modulus is given by

$$k^2 = 1 - \mu^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (9.24)$$

and the argument by $\psi = \lambda_0 \omega t. \quad . \quad . \quad . \quad . \quad . \quad . \quad (9.25)$

Comparison with (6.4) and (6.23) shows that

$$V = \tfrac{1}{2} R \omega (1 - \mu^2) \lambda_0^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (9.26)$$

$$u = R \omega \lambda_0^2 [\operatorname{dn}^2 \psi - \tfrac{1}{2} (1 + \mu^2)]. \quad . \quad . \quad . \quad (9.27)$$

The longitude ϕ is found from the equation

$$\phi = \lambda_0 \left[\operatorname{zn} \psi + \left\{ \frac{E}{K} - \tfrac{1}{2} (1 + \mu^2) \right\} \psi \right]. \quad . \quad . \quad (9.3)$$

The period for the velocity is given by $\psi = 2K$, and the change in longitude during the period is therefore

$$\lambda_0 [(1 + \mu^2)K - 2E] \text{ towards the west.} \quad . \quad (9.31)$$

10. Numerical Examples.

In the following examples the velocity of the moving particle is taken as 10 metres per second. The dimensions

and period of rotation of the smooth level globe are those of the earth. Thus we have

$$V = 10 \text{ m./s.} = 864 \text{ km./day} \quad . \quad . \quad (10.1)$$

$$\omega R = 4 \times 10^4 \text{ km./day} \quad . \quad . \quad . \quad (10.2)$$

$$\frac{V}{\omega R} = .0216 \quad \text{and} \quad \frac{\omega R}{V} = 46. \quad . \quad . \quad (10.3)$$

Case I. a.— $\lambda_0 = 0$. The particle is projected along the equator from west to east and continues to move along the equator.

Case I. b.—When λ_0 is small, μ is large and k is small. The elliptic functions may be represented with sufficient accuracy by circular functions, as in the analogous case of the pendulum.

Here

$$\lambda = \lambda_0 \cos \left(\sqrt{\frac{2V\omega}{R}} \cdot t \right),$$

$$\phi = Vt/R.$$

The period $= 2\pi \sqrt{\frac{R}{2V\omega}} = 4.8 \text{ days.}$

The wave-length $= 4160 \text{ km.}$

Case I. c.—As λ_0 is increased, the angle at which the equator is crossed is increased. If the equator is crossed at right angles $\alpha = \frac{\pi}{2}$ and therefore $\mu = 1$, $k = 1/\sqrt{2}$.

The tables give $E = 1.351$, $K = 1.854$, and hence the formulæ (7.6), (7.32), (7.5) show that the period $= 136 \text{ hours} = 5.7 \text{ days}$, the wave-length $= 2240 \text{ km.}$, and the amplitude $R\lambda_0 = 935 \text{ km.}$

Case I. d.—If λ_0 is increased still further, the equator is crossed in the retrograde direction. The distance between successive crossings is reduced. The distance vanishes when the relation between the elliptic integrals is $E = \frac{1}{2}K$. The track is now a figure of eight. The solution of the equation $E = \frac{1}{2}K$ is $k = \sin 65^\circ.35 = .909$. This gives us $\mu = .459$, $R\lambda_0 = 1200 \text{ km.}$, and the equator is crossed at $130^\circ.7$. The period (found by writing $K = 2.321$ in (7.6)) is 7.1 days or 170 hours*.

* The solution of $E = \frac{1}{2}K$ is given by Hess (*l. c.* p. 27) and Love (*l. c.* p. 53) as $k = \sin 64^\circ.65$. Comparison with Legendre's Tables (*Fonctions Elliptiques*, table viii. p. 290) shows that the correct solution is that given above.

Fig. 2.

CASE 1A.

STEADY MOTION ALONG THE EQUATOR.



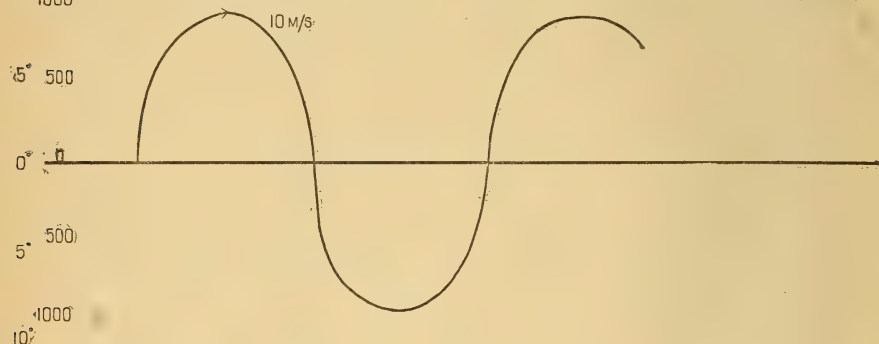
CASE 1B.

NEAR THE EQUATOR CURVE OF STILES. PERIOD 116 HOURS. WAVE LENGTH=4,160 KM.



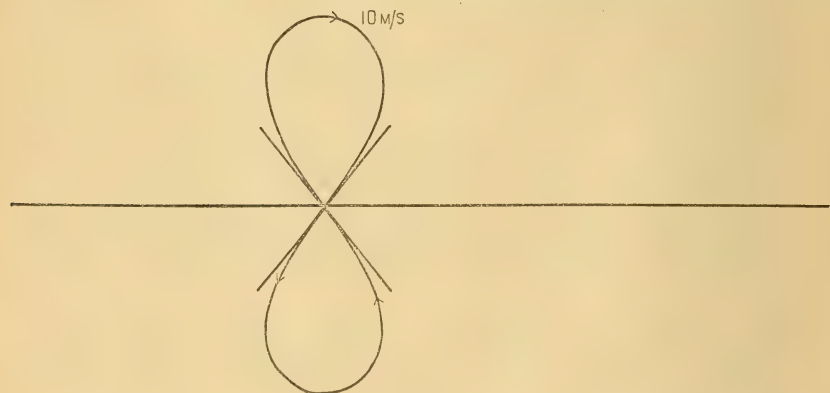
CASE 1c.

EQUATOR CROSSED AT RIGHT ANGLES. PERIOD 136 HOURS. WAVE LENGTH = 2,240 KM.



CASE 1d.

EQUATOR CROSSED AT 131° PERIOD = 170 HOURS. REENTRANT PATH.



Case I. e.—Further increase of λ_0 leads to looped tracks in which the motion is, on the whole, from east to west. As an example, we take the case in which the equator is crossed at 150° .

$$\mu = \cot 75^\circ = \cdot 268, \quad \lambda_0 = \sqrt{\frac{2V}{R\omega}} \sin 75^\circ = \cdot 201,$$

$$\lambda_0 R = 1280 \text{ km.}, \quad k = \sin 75^\circ = \cdot 966.$$

The tables give $K = 2\cdot 7681$, $E = 1\cdot 0764$.

Hence by (7.6) and (7.32) the period $= 203 \text{ hr.} \doteq 8\frac{1}{2} \text{ days}$ and the wave-length $= 1630 \text{ km.}$

To determine the size of the loops we require the positions of the double points. These are found by solving the equation

$$\text{zn } \psi + \left(\frac{E}{K} - \frac{1}{2} \right) \psi = 0,$$

obtained by writing $\phi = 0$ in (7.33).

The root is found to be approximately $\psi = 2\cdot 03$. The latitude of the double points is given by

$$\lambda = \lambda_0 \text{cn } \psi = \cdot 208 \lambda_0.$$

Hence $\lambda R = 266 \text{ km.}$

The width of a loop can be determined by investigating the points where u , the easterly component of the velocity, vanishes. The condition (derived from (7.27)) may be expressed in the form

$$\text{cn } \psi = \left[\frac{1}{2}(1 - \mu^2) \right]^{1/2}.$$

This equation is satisfied in this particular case by $\psi = \frac{1}{3}K$, and on substitution in (7.33) we find that the half-width of the loop is 368 km.

Case II.—As the interval between the loops is increased, we approach the limiting case in which the equator is asymptotic to the track.

In this case $\lambda_0 = \sqrt{\frac{2V}{R\omega}} = \cdot 208$ (by writing $\alpha = \pi$ in (7.5)), and therefore $\lambda_0 R = 1324 \text{ km.}$

To determine the size of the loop, its width and also the position of the double point must be found. To find the

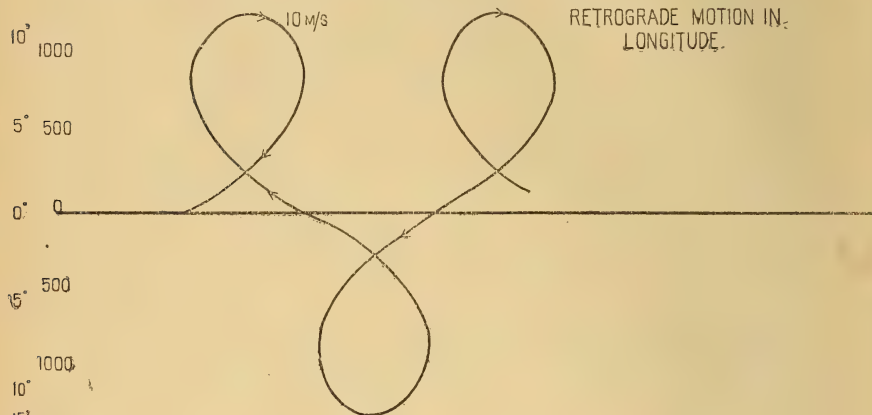
width we determine the points at which the motion is north or south by solving the equation (8.22)

$$\frac{d\phi}{d\psi} = \omega\lambda_0^2 [\operatorname{sech}^2 \psi - \tfrac{1}{2}] = 0.$$

Fig. 3.

CASE I_c.

EQUATOR CROSSED AT 150°. PERIOD=203 HOURS. WAVE LENGTH 1,630 KM.

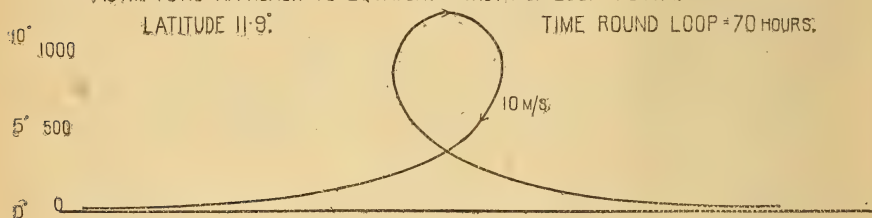


CASE II.

ASYMPTOTIC APPROACH TO EQUATOR. WIDTH OF LOOP 704 KM.

LATITUDE 11.9°.

TIME ROUND LOOP = 70 HOURS.



CASE IIIA.

APPROXIMATELY CIRCULAR PATH WITH DRIFT TO WEST 150KM. EACH REVOLUTION.
LATITUDE 16.85°

LATITUDE 11.9°

WIDTH OF LOOP 482KM. E. AND W. FROM N. CURRENT TO S.
632KM. FROM S. CURRENT TO N.

RANGE N. AND S. 550KM.

0° 500

The smallest positive root is $\psi = .881$ and, for this value of ψ , $\tanh \psi = 1/\sqrt{2} = .707$. Accordingly, the half-width is

$$R\phi = R\lambda_0 [\tanh \psi - \tfrac{1}{2}\psi] = 1324 \times .266 \text{ km.} \\ = 352 \text{ km.}$$

The position of the double point is found by solving

$$\tanh \psi = \tfrac{1}{2}\psi.$$

The positive root of this equation is $\psi = 1.915$, which corresponds with $\lambda = .2884\lambda_0$ and $R\lambda = 382 \text{ km.}$

The tangents at the double point are inclined to the meridian at an angle

$$\cos^{-1} (2 \sinh \psi \operatorname{sech}^2 \psi), \text{ where } \psi = 1.915.$$

This angle is equal to $56^\circ.5$.

The time taken in describing the loop is $2\psi/\lambda_0\omega$, or 2.9 days.

Case III.—If the particle is projected eastwards at 10 m./s. at a point whose distance from the equator exceeds 1324 km. the track lies entirely in one hemisphere and consists of loops.

A simple example is found by choosing μ in the notation of § 9 as $1/\sqrt{2}$. It follows that

$$k = 1/\sqrt{2}, \quad \lambda_0 = \sqrt{\frac{4V}{R\omega}} = .294, \quad \mu\lambda_0 = .208,$$

$$\lambda_0 R = 1870 \text{ km.} \quad \text{and} \quad \mu\lambda_0 R = 1320 \text{ km.}$$

The last two of these data are the distances from the equator of the points where the motion is eastwards and westwards respectively.

The period for the velocity is $2K/\lambda_0\omega$ or 48 hr. This is the time from the north of one loop to the north of the next.

The change in longitude during this period is

$$\lambda_0 [(1 + \mu^2)K - 2E] \text{ towards the west.}$$

On substitution of the values of E and K , viz. $E = 1.3506$ and $K = 1.8541$, we find that the distance between the most northerly points of successive loops is 150 km.

The positions of the double points, which have the

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same longitudes as the most northerly points, are found by solving

$$\operatorname{zn} \psi = \left(\frac{3}{4} - \frac{E}{K} \right) \psi$$

$$\text{or} \quad \operatorname{zn} \psi = \cdot 0215 \psi.$$

The positive root is $\psi = 1\cdot69$.

The distance from the equator of the double point is

$$R\lambda_0 \operatorname{dn}(1\cdot69) = 1330 \text{ km.}$$

To find the width of the loop we proceed as in Case II. above. From equation (9·27) the most easterly point of a loop is given by

$$\operatorname{dn}^2 \psi - \frac{3}{4} = 0.$$

$$\text{This is equivalent to} \quad \operatorname{sn} \psi = \frac{1}{\sqrt{2}},$$

$$\text{and hence from the tables} \quad \psi = \frac{4\cdot01}{9} K = \cdot 826.$$

The difference of longitude between the most northerly and the most easterly point of a loop, found by substituting the value of ψ in the formula (9·3)

$$R\phi = R\lambda_0 (\operatorname{zn} \psi - \cdot 0215 \psi),$$

is 241 km.

It has been shown already that the displacement from loop to loop is 150 km. Hence the width of a loop measured from a point where the particle is going north to the next point where it is going south is 482 km., whilst the distance from the latter point to the next one where it is going north is 632 km.

11. The formulæ which have been used in the foregoing investigation are only approximate, and it would not be right to use them in higher latitudes. It is evident, however, that the loops will become more nearly circular as the poles are approached. The classification may be extended to distinguish :

Case III. a.—Loops not passing through or including the pole.

b.—Loops passing through the pole.

c.—Loops surrounding the pole, pole not central.

d.—A circle of latitude.

12. The classification which has been adopted for the tracks of particles moving at 10 m./s. holds good for all velocities comparable with wind-velocities and therefore of practical interest. It may be noted, however, that for sufficiently great velocities the classification would break down. Cases III. *a*, *b*, and Case II. become identical for the path which crosses the pole and is asymptotic to the equator. Such a particle tends to a position of rest relative to axes fixed in space, and it follows that the velocity of projection from the pole must be equal to the absolute velocity of a point on the equator.

Cases III. *c* and *d* are possible when the relative velocity does not exceed twice the absolute velocity of a point on the equator. For velocities above that limit all tracks cross the equator.

XLV. Notes on the Absorption of X-Rays.

By TYCHO E:SON AURÉN, *Dr. phil.**

I. Introduction.

THE coefficient (μ) for the absorption of X-rays is found by means of the law

$$I = I_0 e^{-\mu d}, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where I_0 is the intensity of the incident rays, I that of transmitted rays, and d the thickness of the sheet of a definite material. As the above law only holds under the condition that radiation is homogeneous, and a perfectly homogeneous radiation of sufficient intensity is not easily brought about, there arise, already from this cause, serious difficulties as to the exact determination of absorption coefficients. Moreover, other difficulties are presented by the fact that the intensity of radiation in the bulb is continually changing, and that the intensity of the rays will be diminished not only by absorption but also by scattering. Thus the determinations made, up to this date, of absolute absorption coefficients seem to be rather uncertain†. Nowadays, the ratio of absorption is

expressed by the mass-absorption coefficient ($\frac{\mu}{\sigma}$), which is obtained by dividing the absorption coefficients by the density (σ) of the absorbing material.

W. H. Bragg and Pierce† have, instead of the coefficient

* Communicated by the Author.

† Compare Bragg and Pierce, *Phil. Mag.* xxviii. p. 626 (1914).

just mentioned, made use of the atomic absorption coefficient that expresses the proportion of the energy of an X-ray pencil which is absorbed on crossing a surface on which lies one atom to every square centimetre. This kind of expression will in many cases be preferable to the mass-absorption coefficient, because the atomic absorption coefficient can be more easily than that coefficient compared with other characteristic constants of the atom. As the mass of an atom can be easily calculated $\frac{\mu}{\sigma}$ is obtained by dividing the atomic absorption coefficient by the mass of the corresponding atoms.

The relation of the absorption coefficient and the wavelength (λ) can be expressed approximately by the formula

$$\frac{\mu}{\sigma} = A\lambda^x, \dots \dots \dots (2)$$

where A and x are constants. x seems to have the same value (about 3) in all materials.

The relation of the atomic absorption coefficient (α) and the atomic number is given by Bragg and Pierce in the formula

$$\alpha = CN^4\lambda^{5/2}, \dots \dots \dots (3)$$

where C is a constant and N the atomic number.

From the formula (2), it follows that the ratio of the absorption coefficients of two materials must be constant, *i. e.* independent of the wave-length, and according to the formula (3), this ratio might be expressed by the ratio of the fourth powers of the atomic numbers of the respective elements. The fact that the ratio in question is really constant in the case of rays of widely different wave-lengths was first pointed out by Barkla and Sadler * and, later on, it has been confirmed by Bragg and Pierce †.

In the following table, the values found by the last-named scientists for the ratio of the atomic absorption coefficients of a few elements are compared partly with the corresponding values which I have calculated from the values found by Barkla and Sadler of the mass-absorption coefficients, partly with the values I have found by means of the method mentioned below. In column 1 are noted the average values found by Bragg and Pierce by means of the characteristic rays from Ag, Rh, Pd; in column 2, those found by Barkla and Sadler by similar radiation from Ag; and in

* Barkla and Sadler, *Phil. Mag.* xvii. p. 739 (1909).

† Bragg and Pierce, *loc. cit.*

column 3, those found by the same scientists by characteristic radiation from Cr, Fe, and Co; and in column 4, those found by myself, by using non-homogeneous rays from an X-ray bulb with an anticathode of tungsten which have been filtered through an aluminium screen:—

TABLE I.

| Elements. | 1. Bragg and Pierce with rays from Ag, Rh, Pd. | 2. 3. Barkla and Sadler with rays from | | 4. Aurén with non- homogeneous rays. |
|-------------|---|---|-------------|--|
| | | Ag. | Cr, Fe, Co. | |
| Fe/Al..... | 15.2 | 14.3 | 1.69 | 13.4 |
| Ni/Fe..... | 1.30 | 1.37 | 1.22 | 1.30 |
| Cu/Ni | 1.17 | 1.15 | 1.21 | 1.10 |
| Zn/Cu | 1.13 | 1.14 | 1.22 | 1.15 |
| Pt/Al..... | 163 | 163 | 27.7 | 156 |
| Pt/Ag..... | 7.64 | 7.69 | 1.61 | 1.76 |
| Sn/Ag..... | 1.33 | 1.37 | 1.37 | 1.04 |
| Au/Pt | 1.05 | 1.10 | [1.06] | 1.02* |
| Au/Cu | 7.28 | 7.86 | [11.8] | 8.29* |

* Au=540 from curve, fig. 2.

The agreement between the various experiments is, on the whole, remarkably good, and where sensible changes have been observed they may easily be accounted for. Within the range of selective absorption, this law does not hold, and, from what I have found, neither does it hold when rays of greater wave-length (soft rays) are examined. Though the agreement between the values of the first, second, and fourth columns, in all cases but one, is good, the values of the third column differ from those in regard to the combinations Fe/Al and Pt/Al, which are too low. As for the combination Pt/Ag, the values in the first and second columns agree between themselves, but these values do not agree with the values in the third and fourth columns, which, on the other hand, closely agree between themselves. The cause of the want of agreement between the said couples certainly depends on the fact that one of the constituent metals of the combination enters into the range of selective absorption in using the radiation in question. As it appears from the experiments of Barkla and Sadler, it is not here the case that the relation between the absorption coefficients is independent of the wave-length.

The ratio of the atomic and molecular absorption coefficients respectively is, in the ensuing pages, expressed by

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X. a. k. and X. m. k., and the absorption coefficient of the element in question is always compared with the absorption coefficient for *water*. Since, as shown above, the relative absorption coefficients are independent of the wave-length, and so are more easily to be exactly determined than the absolute absorption coefficients, and since they, as a rule, in different elements, plainly differ from each other, the relative atomic or molecular absorption coefficients may probably very well have the faculty of characterizing different species of atoms or molecules.

In making the inquiries which I am going to describe in the following pages I have tried to determine the relative absorption coefficients for several elements. As it has been found possible to determine the wanted constants in solutions, and as many elements are attainable without difficulty in the form of solutions, whereas they cannot at all or only with difficulty be obtained in solid or gaseous state, under conditions to allow the examining of absorption, I have chiefly made use of solutions. From the many experiments made on the absorption of X-rays, we infer that, "Though the experiments undertaken in cases of different density, temperature, and chemical combination may not nearly possess the required degree of experimental accuracy so as to eliminate every influence on absorbability, it may be stated as certain that the power of absorption is essentially determined by the properties of the atom"*. In calculating the relative atomic absorption coefficients from the values of the molecular absorption coefficients of the elements examined, I have, consequently, started from the principle that the absorption of the solution is additively determined by the absorption of the constituent atoms.

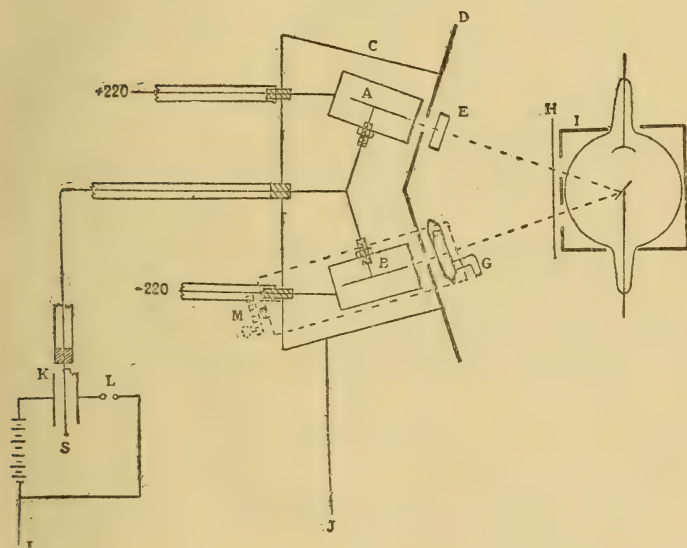
II. *Method of Investigation.*

In order to exclude errors due to incessant changes in hardness and intensity of the radiation, as well as only to have to make null-point-adjustments, my experiments have been arranged in the following manner. Two pencils of rays have been made to pass, one through the element the X. m. k. of which is to be determined, and the other through a sheet of water the thickness of which could be varied. The thickness of the water sheet is regulated so that the intensity of both the pencils of rays is equally great. This, on the other hand, can be determined by observing when the currents of saturation in two ionization-chambers, into which

* Pohl, *Die Physik der Röntgenstrahlen*, p. 91 (1912).

the two pencils of rays are allowed to penetrate, become equally strong. By combining the ionization-chambers with each other so as to make the two saturation currents neutralize each other, the null-point method can be used. After determining the thickness of the water sheet the relation between the absorption coefficients of the element examined and of water is easily found. The experimental arrangements are more plainly made out by the

Fig. 1.



schematic figure (fig. 1) above. The two ionization-chambers (A and B), consisting of metallic boxes, in which as electrodes, insulated from the boxes by sulphur, metal sheets are fixed, and each of which is supplied with a mica window (2.5 cm. diam.), are, by way of avoiding influence from the bulb and from the high-tension wires, placed in a large earthen metal box (C), the front of which is a lead screen (D). Just in front of the said mica windows, apertures are made in the lead screen, and before these, there are two absorption vessels (E and F) at a distance of 4 cm. from the respective ionization-chambers. In one of these are the parallel walls, bounding the liquid sheet to be examined, at a distance of 1 cm. from each other, and made of thin mica, whereas the other walls are made of glass. The vessel

is furnished with two additional pipes, one in the lower and the other in the upper part of it. By means of a short tubing the lower one is connected with a vessel containing the liquid to be examined. The other pipe is applied for the purpose of sucking up the liquid into the vessel. The other absorption vessel, that in what follows is designated as the comparator (F), consists of two parallel brass laminæ, provided with round apertures (3 cm. diam.), covered with thin mica, and the borders of these laminæ are connected by rubber cloth so that a water-tight bag is obtained. To the front lamina is applied an additional tube (G), that communicates by a rubber tube with a water-cistern, from which the vessel is supplied with water. The two brass laminæ are firmly fixed in a dividing machine (M), so that by the aid of the screw of the machine they may be caused to slide on each other, and so the thickness of the water be changed, and this change be accurately determined. The bulb, consisting of a Siemens tungsten tube with fin radiator for cooling the anticathode, through which passes a current of 0.5–1 milliamperes, is placed in a box (I), coated with lead, and furnished with two apertures directly in front of the two absorption vessels. For the purpose of filtering, an aluminium screen (H) 1.25 mm. thick is applied. The ionization-chambers are charged up to +220 and –220 volts respectively, and the electrodes in them are connected with each other as well as with a string-electrometer (K) of Lutz-Edelmann, in which there is a Pt-string of 0.001 mm. thickness. The sensibility of the electrometer amounted to about 1 volt for one division of the scale. All the conductors are protected by metal tubes, which are earthed (J), and the electrometer-string (S) also, by means of a simple key (L), can be earthed. As current source for the bulb, I have used a high-tension transformer of Siemens' construction.

The determinations were carried out in the following manner. The absorption vessel is first filled with water, whereupon this, as well as the water-filled comparator, was exposed to radiation. The electrometer-string having been momentarily earthed, it is observed to which side the string seems to be moving. By augmenting or diminishing the thickness of the water-sheet in the comparator, radiation in the two ionization-chambers can be made to be equal in strength, in which case the currents neutralize each other, and the electrometer-string will remain at rest. The position of the screw (d_1) is read, whereupon the water of the absorption vessel is exchanged for the solution whose absorption coefficient has to be determined, the comparator is

readjusted, and the position (d_2) of the screw is read again. The change of the thickness of the water-sheet ($d_2 - d_1$) depends evidently on the difference of absorption in the solution and of a water-sheet of the same thickness (1 cm.). If we suppose the intensity of the incident rays at the absorption vessel to be I and at the comparator kI , and the absorption coefficients of water and the solution to be μ_w and μ_s respectively, then it follows, after the first adjustment, that

$$Ie^{-\mu_w} = kIe^{-\mu_w d_1},$$

and after the second adjustment, that

$$Ie^{-\mu_s} = kIe^{-\mu_w d_2},$$

whence it follows that

$$\mu_s - \mu_w = \mu_w(d_2 - d_1);$$

or, when the absorption coefficient of the dissolved substance (μ_x) = $\mu_s - \mu_w$,

$$\frac{\mu_x}{\mu_w} = d_2 - d_1.$$

Now X. m. k. (ρ) is readily found if the number of molecules in one litre is calculated. Since pure water contains 55.5 gram-molecules H_2O , and the solution m gram-molecules of the dissolved substance per litre, we obtain

$$\rho = \frac{(d_2 - d_1)55.5}{m}. \quad . \quad . \quad . \quad . \quad (4)$$

This formula presupposes that the water quantum of the solution is the same as that of pure water, which case only can be thought correct when working with diluted solutions. When working with highly concentrated solutions, a correction for the wanting water quantum must be made. This correction is readily calculated when the specific weight of the solution is known. The value of d_2 is augmented by the thickness of the water sheet that should be added in order to keep the water quantum of the absorption vessel unaltered. Although, no doubt, part of the rays, scattered from the absorption vessels, have penetrated into the ionization-chambers, no special correction of the fault originating from this source has been made. The intensity of the scattered rays must needs be thought almost equal, because the density of the solutions has very nearly been the same as that of water and the mass-scattering coefficients of light substances within wide limits are independent of the

wave-lengths, as shown by the experiments of Barkla. When making controlling experiments, the absorption vessels being placed at a distance of 16 cm. from the ionization-chambers, the same values of ρ have, within experimental error, been observed.

Although the equation (1) whence (4) is deduced only holds when the radiation is homogeneous, this formula, according to Barkla's law, confirmed by various experiments (pp. 472-473) must hold as well when non-homogeneous radiation is used, supposing that the wave-lengths of the rays are not the same or nearly the same as those of the characteristic radiation of the element to be examined, and that rays of too great a wave-length are not used.

In the radiation used by the author from a bulb with an anticathode of tungsten, and with a spark-gap of at least 10 cm., the rays have been filtered through an aluminium screen 1.25 mm. thick. By the heterogeneous radiation, the rays of a greater wave-length have thus been filtered away, and the rest must certainly have got a decided maximum of intensity. When heterogeneous rays from a bulb with a spark-gap of some centimetres are transmitted by an aluminium screen sufficiently thick, the passing rays may practically be considered as homogeneous*. When changing the spark-length at the bulb, there has not in any case been observed either in lighter or heavier substances any influence on the determinations of the relative atomic absorption coefficients. Within the range of the wave-lengths used by the author, the determinations of these coefficients are independent of the wave-length, and thus Barkla's law must be applicable.

By determining in the ordinary way the thickness of the aluminium sheet necessary to diminish the ionization by about half, the absorbability of radiation could, by means of formula (1), approximately be determined. Thus the approximate wave-length could be evaluated†, and as a mean value $\lambda = 0.35 \cdot 10^{-8}$ was obtained. Among the substances examined certainly W, and probably also Ce and Ba, have entered into the range of selective absorption.

The rays I have made use of have not been homogeneous, it is true, but in determining X. a. k., with regard to absorption for different sheet thicknesses, they have behaved in the same way as if they had been homogeneous. Indeed, it appears

* Compare Kaye, 'X-Rays,' London, 1914, p. 103.

† Barkla and Dunlop, Phil. Mag. xxxi. p. 229 (1916).

from the experiment, exhibited in the following table, that X. a. k. for aluminium is independent of the thickness of the absorbing screen.

TABLE II.

| Thickness of aluminium screen in cm. (a). | Thickness of water sheet in cm. ($d_2 - d_1$). | X. a. k. $= \frac{(d_2 - d_1) 55.5}{a.m.}$ |
|---|--|---|
| 0.06 | 0.38 | 3.5 |
| 0.09 | 0.60 | 3.7 |
| 0.11 | 0.71 | 3.6 |
| 0.25 | 1.51 | 3.3 |
| Mean 3.5 | | |

In the following table there is exhibited as a proof a series of observations, respecting absorption in aqueous solutions of KCl of various concentrations.

TABLE III.

| Spec. weight. | Number of gram-molecules KCl pr l.(m.). | Thickness of water sheet in cm. ($d_2 - d_1$). | | X, m. k. |
|---------------------|---|--|-------|----------|
| | | obs. | corr. | |
| 1.1515 | 3.59 | 1.06 | 1.18 | 18.2 |
| 1.1260 | 2.84 | 0.98 | 1.07 | 20.9 |
| 1.1088 | 2.46 | 0.87 | 0.94 | 21.3 |
| 1.0897 | 2.02 | 0.67 | 0.73 | 20.0 |
| 1.0740 | 1.68 | 0.56 | 0.61 | 20.1 |
| 1.0540 | 1.22 | 0.49 | 0.52 | 23.6 |
| 1.0396 | 0.88 | 0.27 | 0.29 | 18.3 |
| 1.0189 | 0.43 | 0.16 | 0.18 | 23.2 |
| Mean 20.7 ± 0.5 | | | | |

The agreement between the values of X. m. k. found in the various concentrations (which in other experiments have, as a rule, been greater than in the above instance), is, as is shown here, rather good. The special values, from which the average values of Table IV. are calculated, generally differ at the most by 5 per cent. from the average numbers. The values of X. m. k., measured after this method, are, as shown in Table III., within experimental error independent of concentration in the solutions to be examined, apart from colloidal solutions. The fact is that for solutions that are strongly hydrolyzed, and then partly pass into a colloidal state, *e. g.* FeSO_4 that has been oxidized by the contact of air, Na_2HAsO_4 , &c., absorption increases with increased dilution, about which see further on (p. 485). The concentration of the examined solutions has mainly been chosen so that $(d_2 - d_1)$ has, at the utmost, reached about 1.5 cm. by the way of avoiding the correction necessitated if the position of the comparator is too much changed relatively to the bulb.

When elements insoluble in water have been investigated, especially organic fluids whose absorption is less than that of water, another absorption vessel containing a water sheet of 1 cm. thickness has been placed before the absorption vessel. Then absorption has been examined when this vessel has been empty, as well as when it has been filled with a liquid. After reading the thickness of the water sheet $(d_2 - d_1)$ in the comparator, we directly find the thickness of the water sheet that corresponds to a sheet of liquid in question 1 cm. thick. In examining absorption for metals, the procedure has been similar.

III. *Results of Experiments.*

The following table gives a survey of the values of X. m. k. I have found when examining the solutions named in the table. For each substance, as a rule, I have carried out 6–8 determinations with various concentrations or, if this has not proved possible, several determinations for the concentration, and the values seen in the table are average values of these determinations.

TABLE IV.

| Substance. | Concentration in gram- molecules pr l. | X. m. k. |
|---|--|----------|
| NaClO ₃ | 3—1.01 | 14.2 |
| NaCl | 3.38—0.43 | 11.5 |
| NaOH | 16.75 | 2.77 |
| C ₆ H ₆ (Benzene)..... | 11.3 | 2.97 |
| CH ₄ O (Methyl alcohol) .. | 25.0 | 1.56 |
| C ₄ H ₁₀ O (Butyl alcohol) .. | 10.9 | 3.32 |
| C ₃ H ₆ O (Acetone) | 13.7 | 2.58 |
| C ₄ H ₁₀ O (Ethyl ether) | 9.68 | 3.31 |
| C ₃ H ₈ O (Propyl alcohol) ... | 13.45 | 2.69 |
| (C ₂ H ₅) ₄ Si | 5.27 | 8.56 |
| (C ₆ H ₅)Si(CH ₃) ₃ | 5.76 | 9.06 |
| HNO ₃ | 4.0 | 3.36 |
| H ₄ NNO ₃ | 1.85 | 4.17 |
| C ₆ H ₅ NO ₂ (Nitro-benzene) . | 9.82 | 5.40 |
| C ₅ H ₅ N (Pyridine) | 12.5 | 3.14 |
| C ₆ H ₅ NH ₂ (Aniline) | 8.05 | 3.63 |
| MgCl ₂ | 3.68—0.92 | 22.5 |
| Al ₂ (SO ₄) ₃ | 0.97—0.21 | 41.0 |
| H ₃ PO ₄ | 5.73—2.80 | 9.43 |
| H ₂ SO ₄ | 4.0 —1.0 | 11.48 |
| HCl | 4.72—1.78 | 9.55 |
| KCl | 3.59—0.43 | 20.7 |
| CaCl ₂ | 2.48—0.62 | 33.4 |
| CrCl ₃ | 1.0 —0.25 | 52.6 |
| MnCl ₂ | 0.99—0.24 | 60.4 |
| KFe(SO ₄) ₂ | 0.48—0.24 | 79.4 |
| NiCl ₂ | 1.0 —0.25 | 78.4 |
| CoCl ₂ | 1.0 —0.25 | 72.9 |
| CuCl ₂ | 1.0 —0.13 | 84.1 |
| ZnCl ₂ | 1.0 —0.25 | 96.3 |
| ZnSO ₄ | 1.0 —0.14 | 84.8 |
| Na ₂ HAsO ₄ | 1.0 | 136 |
| KBr | 0.53—0.46 | 165 |
| SrCl ₂ | 0.4 —0.14 | 192 |
| MO ₄ (+3.85 m. HCl) | 0.13 | 246 |
| AgNO ₃ | 0.27—0.034 | 303 |
| CdCl ₂ | 0.26—0.033 | 320 |
| NaI | 0.25—0.063 | 317 |
| BaCl ₂ | 0.25—0.031 | 353 |
| Na ₂ WO ₄ | 0.2 —0.05 | 316 |
| H ₂ PtCl ₆ | 0.035 | 586 |
| HgNO ₃ | 0.125—0.031 | 550 |
| Pb(NO ₃) ₂ | 0.125 | 576 |
| Bi(NO ₃) ₃ | 0.08—0.02 | 687 |
| U(SO ₄) ₂ | 0.05—0.013 | 1146 |

Table V. shows a survey of the values of X. a. k. I have found when examining metals in a solid state.

TABLE V.

| Metal. | Thickness of metal sheet in cm. | X. a. k. |
|----------|---------------------------------------|----------|
| Al | 0.06—0.25 | 3.5 |
| Fe | 0.005 | 47.3 |
| Ni | 0.01 | 57.0 |
| Cu | 0.006 | 65.4 |
| Sn | 0.0047 | 311 |

The relative atomic absorption coefficients of the elements that are components of the combinations seen in Table IV. have been calculated and brought together in Table VI. In these calculations, I have started from the values of X. a. k. for oxygen and hydrogen, which are readily obtainable from the determinations of X. m. k. for NaClO_3 , NaCl , and H_2O . The difference between the values for the former combinations is 2.7; and as this difference depends on 3 atoms of oxygen, the X. a. k. of oxygen will be 0.9. Since X. m. k. of water is 1.0, we likewise find the value of X. a. k. of hydrogen to be 0.05. By the intermediary of the values of oxygen and hydrogen, we can then easily find X. a. k. for Cl from HCl , for S from H_2SO_4 , for N from HNO_3 , &c., whereupon the values of X. m. k. for the combinations X. a. k. for the other elements have been calculated in the same way. After examining two or more substances, from which the value of X. a. k. for a certain element has been calculated, the especial values as well as the mean value have been given. The table, moreover, gives the so-called atomic numbers, in which case I have used the numbers that of late years have been in common practice (Moseley, Rutherford, &c.).

Apart from the deviations in Co and W, X. a. k. steadily increases along with the increasing atomic weight.

As to the deviation for W, it certainly depends, as shown before, on selective absorption. In relation to X-rays, Ni appears to occupy the place between Co and Cu, accordingly not the place due to its atomic weight*, and from a chemical

* Compare Pohl, *Die Physik der Röntgenstrahlen*; Moseley, *Phil. Mag.* xxvi. p. 1031 (1913); Barkla, *Phil. Mag.* xiv. p. 408 (1907).

TABLE VI.

| Atomic number. | Elements. | X. a. k. | Substances examined. |
|----------------|-----------|----------|--|
| 1 | H | 0.05 | |
| 6 | C | 0.46 | Methyl Alcohol... 0.46 Butyl alcohol ... 0.48 Propyl alcohol ... 0.46 Acetone 0.46 Ethyl ether 0.48 Benzene 0.45 Aniline 0.44 Pyridine..... 0.45 Nitro-benzene ... 0.45 HNO ₃ 0.61 NH ₄ NO ₃ 0.64 |
| 7 | N | 0.63 | |
| 8 | O | 0.9 | |
| 11 | Na | 1.9 | NaOH 1.8 NaCl 2.0 |
| 12 | Mg | 3.5 | |
| 13 | Al | 3.4 | |
| 14 | Si | 4.1 | (C ₂ H ₅) ₄ Si 3.9 (C ₆ H ₅)Si(CH ₃) ₃ ... 4.2 |
| 15 | P | 5.68 | |
| 16 | S | 7.78 | |
| 17 | Cl | 9.5 | |
| 19 | K | 11.1 | |
| 20 | Ca | 14.4 | |
| 24 | Cr | 24.1 | |
| 25 | Mn | 41.4 | |
| 26 | Fe | 45.5 | |
| 27 | Co | 53.9 | |
| 28 | Ni | 59.4 | |
| 29 | Cu | 65.1 | |
| 30 | Zn | 75.4 | ZnCl ₂ 77.3 ZnSO ₄ 73.4 |
| 33 | As | 128 | |
| 35 | Br | 154 | |
| 38 | Sr | 173 | |
| 42 | Mo | 244 | |
| 47 | Ag | 300 | |
| 48 | Cd | 301 | |
| 50 | Sn | 311 | (Metal.) |
| 52 | I | 315 | |
| 56 | Ba | 334 | |
| 58 | Ce | 327 | |
| 74 | W | 308 | |
| 78 | Pt | 529 | |
| 80 | Hg | 547 | |
| 82 | Pb | 569 | |
| 83 | Bi | 677 | |
| 92 | U | 1123 | |

point of view, there seem to be various reasons why the former place should be appropriate to Ni in the periodical system. X. a. k. for Ni being greater than for Co, is consequently in in good agreement with what is hitherto known about this metal. For Mg and Al I have found approximately the same value of X. a. k., but this certainly depends upon an experimental error, and even a slight one can in this case be rather mischievous, first because the difference between X. a. k. for both metals is a slight one, and again because X. m. k. of the respective salts is mainly determined by the acid radicals.

From the Tables V. and VI. it appears that X. a. k. for Al, Ni, Fe, and Cu has got very closely the same value, whether the values are calculated from the experiments on the respective elements in the metallic state or in the form of salts. From the values for Na and Zn it is clear that X. a. k. is, within experimental error, independent of any chemical combination the constant may be deduced from. These experiments consequently confirm what has been generally admitted in regard to absorption of X-rays: that it does not depend on any state of aggregation or any way of chemical combination.

In the following table there are given the values found by the author for X. m. k. for a solution of FeSO_4 of different concentrations, with the calculated values of X. a. k. for Fe; X. m. k. of the SO_4 ion being, according to the values in in Table VI., 11.4.

TABLE VII.

| Number of gram-molecules per l. | Thickness of water sheet ($d_2 - d_1$). | X. m. k. | X. a. k. |
|---------------------------------------|---|----------|----------|
| 1.08 | 1.03 | 53.0 | 41.6 |
| 0.81 | 0.78 | 53.4 | 42.0 |
| 0.54 | 0.55 | 56.5 | 45.1 |
| 0.41 | 0.42 | 56.8 | 45.4 |
| 0.27 | 0.28 | 57.6 | 46.2 |
| 0.133 | 0.14 | 58.4 | 47.0 |

From the table we see that while concentration is decreasing, the value of X. m. k. is continually increasing, which seems to be owing to the fact that the salt, being

oxidized by the contact of air and hydrolyzed by dilution, partly passes into a colloidal state. As I pointed out earlier, other solutions, that behave in the same way when diluted, display the same property with respect to absorption. The cause of absorption being greater in colloidal solutions seems to be the fact that, as shown by Galecki *, the number of particles irradiating a colloidal solution by X-rays is strongly diminished, in which process part of the radiation energy is required for the disintegration of the particles.

When values for bivalent Fe have been found in greater concentrations, they seem to be more exact than those found at a greater dilution. The mean value, 41.8, of the two first determinations is considered to give the probable value of X. a. k. for bivalent Fe, this value, however, seems to be in reality somewhat too high. The difference between this and the value of trivalent Fe, 45.5, found on examination, is scarcely within experimental error, and, therefore, bivalent Fe is likely to have a lower absorption coefficient than trivalent Fe.

X. a. k. of carbon from cyclic combinations (benzene, aniline, pyridine, nitro-benzene) seems to get a lower value than that of carbon from the alifatic series, which fact may be traced to some difference in the inner structure of the two kinds of carbon. Since, however, as it appears from the figures quoted, a slight uncertainty with respect to X. a. k. of the elements forming combinations with carbon may in a high degree influence the results, there cannot, it seems, at present be drawn any trustworthy conclusions from the differences that have been observed in the measure of the absorption coefficients for different organic combinations. By continued researches the author hopes to be enabled to elucidate this question. As the sensibility of the methods used here can be increased, it will be possible to increase the exactness in determining the relative absorption coefficients.

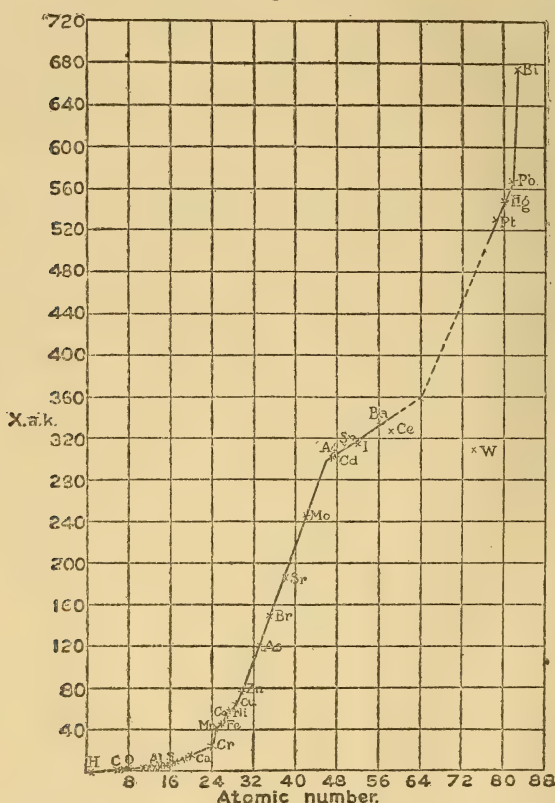
In the same range of ideas, it seems worth noticing that the error in the values found for X. a. k. must be regarded as greater for the elements calculated from combinations whose X. m. k., estimated in percentage, is mostly determined by other component parts of the combinations, *e. g.* Na from NaCl and Al from $\text{Al}_2(\text{SO}_4)_3$.

The comparative slighness of the error is made plain by the good agreement between the values deduced from the above combinations as well as from the same elements in other combinations or in form of metals, *e. g.* for Na from NaOH and for Al from aluminium metal.

* *Kolloidal. Z.* x. p. 149 (1912).

From the different values of X.a.k. I have tried to ascertain for different elements, there is evidence for believing that there exists a simple relation between the above-named quantity for a certain element and the atomic weight or atomic number. According to Bragg and Pierce, the atomic absorption coefficient is thought proportional to the fourth power of the atomic number (3), but after the results brought out by my experiments this cannot hold. Since Bragg and Pierce have only tested a few elements, the lack of agreement in this respect between their results and mine will be easily explicable.

Fig. 2.



The connexion between X.a.k. and the atomic number is graphically brought out in fig. 2, where the atomic number put as abscissa and the corresponding value X.a.k. (Table VI.) as ordinate. The curve displays the values of X. a. k., arranged

in groups, in which the especial values are proportional to the atomic number. Thus the relation between the different groups, on the other hand, appears slightly more complicated.

The elements H-N, O-P, S-Cr, Mn and Fe, Co and Ni, Cu-Pd seem to form fairly well-marked groups. A new group seems to begin at Ag; the elements Pt-Pb seem to belong to a special group, which also seems to be the case with the element U. In order to try to determine whether the atomic absorption coefficient even under other experimental conditions, may be arranged into the same groups, especially at a radiation more homogeneous than that used here, and also with rays of differing hardness, the experiments will be continued.

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for Physical Chemistry.

XLVI. *Normal Anomalies of the Mean Annual Temperature Variation.* By HENRYK ARCTOWSKI*.

THE curves representing annual variations of atmospheric temperature are generally derived from monthly means. For many stations, belonging to different climates, these curves convey the impression of representing a cyclic variation, reflecting, with different amplitudes and more or less retardation, the seasonal changes of solar declination.

If, in the case of long series of observations, instead of monthly means, the averages for each day of the year are taken into consideration, the diagrams thus obtained display most remarkable anomalies. As typical examples I would refer to the curves of Königsberg, Munich, Catania, and Valentia, published by Van Rijckevorsel †, and to the curve derived from observations made in Melbourne, published by R. J. A. Barnard ‡. Because of its simplicity, the Melbourne curve may be taken as a demonstrative example of the problem in view.

From the highest mean temperature, observed in January, the means decrease more or less regularly till the middle of March; then, suddenly, temperature increases about 2° F. Another characteristic break occurs between June 15th and 20th. After the minimum of July the increase of temperature is again interrupted in September and also at the end of November.

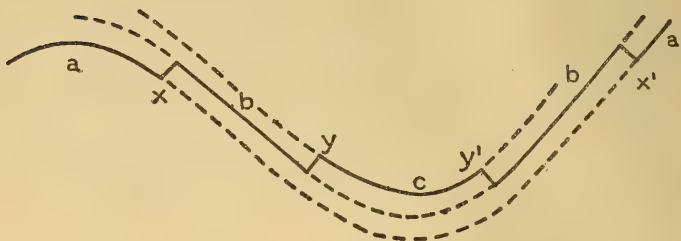
* Communicated by the Author.

† Phil. Mag. ser. 5, vol. xlv. p. 459 (1898).

‡ Phil. Mag. ser. 5, vol. l. p. 408 (1900).

The annual variation for Melbourne may therefore be represented by the following diagram (fig. 1).

Fig. 1.



This diagram expresses graphically the opinion that the seasonal change of temperature in Melbourne is not what it should be; that at given dates of the year (X, Y, Y', X') the natural course of temperature, due to local conditions, is interrupted, just as if the station had been shifted into another climate, similar, but colder than it ought to be during the summer, and warmer than it ought to be during the winter.

The annual variation proceeds by steps. The steps of ascent, occurring while the temperature is decreasing, correspond to similar steps of descent observed during the other half of the year.

Each successive stage marks the passage from one phase to another.

In the preceding example the annual variation is composed of three phases.

This opinion seems never to have been advanced, and it is astonishing to notice that even the fact of the existence of steps during the autumn, corresponding to the steps of the spring, has, so far as I know, attracted practically no attention; though the frequently recurring temperature anomalies for given dates, in May and June, have been very extensively studied.

Researches of particular interest concerning these anomalies are those of G. Hellmann*, W. v. Bezold†, Ch. Dufour‡, W. Martin§, R. Gautier||, and K. Almqvist¶.

* *Ann. d. Phys. u. Chem.* vol. cliv. p. 36 (1876).

† *Abh. math.-phys. Kl. K. Bay. Akad. Wiss.* vol. xiv. II. p. 69 (1883).

‡ *Bull. Soc. Vaud. Sc.* ser. 3, vol. xxix. p. 316 (1893).

§ *Abh. K. Preuss. Met. Inst.* vol. ii. No. 3 (1902).

|| *Arch. Sc. Phys. et Nat.* ser. 4, vol. xxxi. p. 497 (1911).

¶ *Meteor. Zeit.* vol. xxxi. p. 426 (1914).

The principal results gained by these authors may be summarized as follows:—

(1) The temperature depressions are not strictly bound to given dates. Their occurrence varies slightly from year to year, but on the average, in Central Europe, the 11th–15th of May and the 4th–8th of June show a well-pronounced deficiency of temperature.

(2) In all cases, of given years, the comparison of the records has shown a progressive displacement of the wave of cold.

(3) A characteristic distribution of atmospheric pressure over Europe is noticeable. On the ocean a high-pressure area, extending an anticyclonic tongue eastward, moves slowly from the centre of action of the Azores northward.

(4) The resultants of the observed wind directions change radically.

(5) Considering a long series of observations, groups of years may be distinguished for which the temperature depressions of May and June are well pronounced, while in other groups of years they occur only occasionally.

This fact applies at least to the Paris* and Geneva† observations.

The marked departure of temperature conditions of given dates, from the steady seasonal advance, may receive three different interpretations which are illustrated by the following diagram (fig. 2).

Curve “A” expresses the hypothesis that temperature is below the normal for given dates “K,” and that “a'” is the continuation of curve “a.” This represents the very generally admitted hypothesis.

Curve “B” represents the anomaly “p” as being due to such more or less sudden change in the distribution of the isotherms that “b” belongs to a curve identical with “a,” but shifted downwards.

Curve “C” presupposes a radical modification of the annual variation. At “q” the curve “b” is supposed to have a greater amplitude than “a”; at “r” the curve “c” is supposed to have a smaller amplitude than “b.”

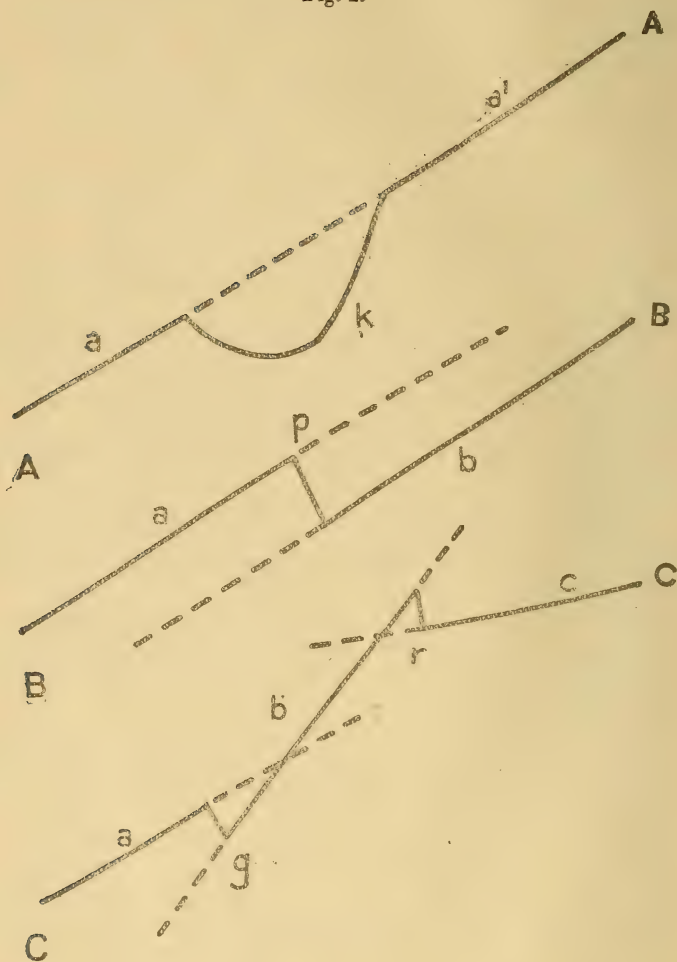
A careful examination of the available temperature curves

* E. Renou, *Annales Bur. Centr. Mét. France*, vol. i. p. B. 195 (1887).

† R. Gautier et H. Duaime, *Arch. Sc. Phys.* ser. 4, vol. xv. p. 545 (1903).

shows that curve "A" may be discarded. On the contrary, curves "B" and "C" must both be taken into consideration.

Fig. 2.



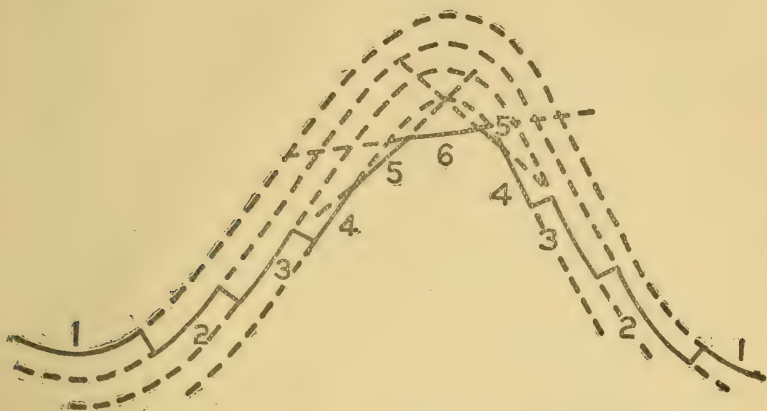
As a typical example I will cite the temperature curve for Warsaw.

The utilized daily means are those of the years 1826-1880*.

* Jan Kowalczyk, *Pam. Fizjogr.*, Warsaw, 1881.

The following diagram (fig. 3) gives an interpretation of the detailed curve.

Fig. 3.



The variation is composed of phases 1, 2, 3, and 4 belonging to four concordant curves. The steps occur approximately at the following dates: Jan. 25, March 9, April 22, Oct. 2, Nov. 29, and Dec. 16.

Then, during the summer, on the contrary, from June 9th till July 28th, we have practically a straight line of mean temperatures increasing from $17^{\circ}6$ to $19^{\circ}3$ C. This line 6 is evidently discordant: it cuts all the others. The summer maximum is 3° below the maximum which would be observed if curve 4 were fully developed. The summer temperature may therefore be considered abnormally low. Now, between 6 and 4 we observe the fragments of a curve 5 extending from May 22nd to June 8th and July 29th to Aug. 26th. This curve intersects all the others: its amplitude is evidently much smaller than the amplitude of curves 1-4.

Although the temperature curve for Warsaw may be considered a most typical example of these normal anomalies of the annual temperature variation, the breaks being too well accentuated to be ascribed to chance circumstances, it is useful to cite a few other examples in order to show how, gradually, we pass from one type of variation to another.

Hellmann has published* a detailed curve of the daily means derived from the observations made in Berlin during the years 1848-1907. Referring to the diagram for Warsaw (fig. 3), the Berlin curve displays the fragments 1-4, 5 is missing, and 6 is a well-developed curve extending from June 13th to Sept. 21st, with a maximum on July 22nd.

* *Preuss. Met. Inst., Abh.* vol. iii. No. 6, Berlin, 1910.

From March 13th to April 7th the increase in temperature is abnormally rapid, so that 3 is discordant with 2 and 4. The drop of temperature between 4 and 6 (June 6–11) is $1^{\circ}5$ C. This is perhaps the most characteristic feature of the curve. Besides, 4 and 6 are discordant. Phase 6 has a smaller amplitude than 4.

Evidently if many curves were available it would be interesting to follow the progressive change from station to station. That these anomalies do not occur simultaneously at different stations but gradually propagate from place to place is a well-established fact, at least for some of the temperature depressions of the spring. The curves for Arcachon, Greenwich, Berlin, Lemberg, Penza, and Wologda, published by Almstedt*, may serve as examples.

Without adopting in their integrity the ideas expressed long ago by Dove†, let us suppose now that the temperature curve for Melbourne, or the curve for Warsaw, or the curves for other places, exhibiting similar anomalies, express the result of an antagonism between maritime and continental climates, respectively characterized by a very small and a very large annual amplitude.

On the ocean, west of the coast of France, the difference between the mean temperatures of the warmest and the coldest day of the year is certainly less than 10° C. In Paris it is $18^{\circ}7$ C., in Warsaw $24^{\circ}7$, in Barnaoul it is $41^{\circ}8$, and the observations of Nertchinsk give $49^{\circ}9$ C. I have traced the curves for Barnaoul (means of the observations made from 1838–1882), and Nertchinsk (1839–1881)‡, and have found, to my great astonishment, that from March 15th to November 1st these two curves are practically identical, whereas during the winter months they differ very greatly one from the other. The winter in Nertchinsk is very much colder than in Barnaoul. The temperatures are:—

| | | Barnaoul. | Nertchinsk. |
|---------|----|-----------------------|-----------------------|
| October | 31 | — $3^{\circ}6$ | — $7^{\circ}2$ |
| January | 2 | — $18^{\circ}3$ | — $30^{\circ}7$ |
| March | 15 | — $10^{\circ}8$ | — $13^{\circ}1$ |

The maxima of the summer are:—

| | | |
|-----------------|---------------|------------------|
| Barnaoul..... | $20^{\circ}2$ | on July the 4th. |
| Nertchinsk..... | $19^{\circ}2$ | „ „ 12th. |

* *Loc. cit.*

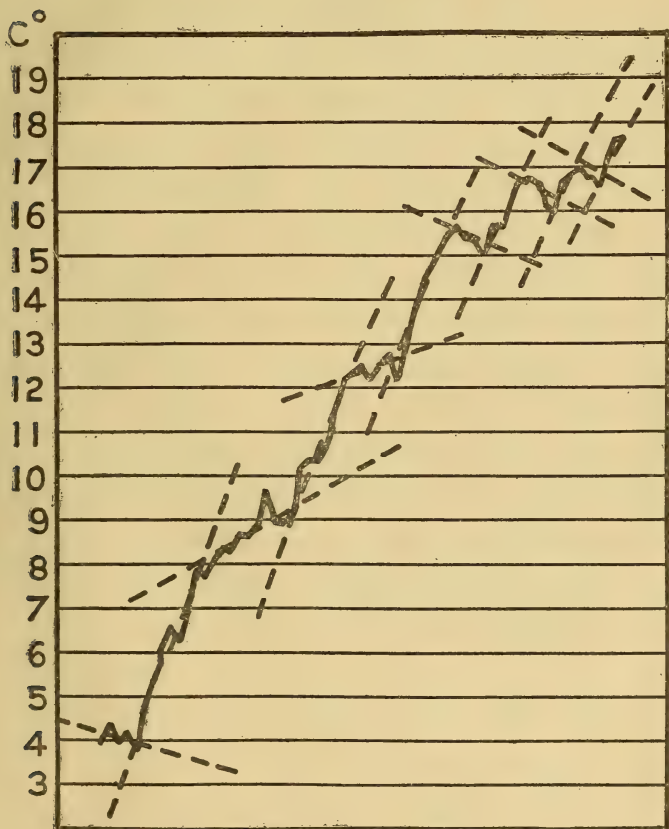
† *Abh. K. Akad. Wiss. Berlin*, p. 121 (1856).

‡ *Repert. f. Meteor. Suppl.* 3, St. Petersburg, 1886.

The temperature curve of Barnaoul belongs therefore to two climates. During the months of April to October it belongs to the excessive continental climate of Nertchinsk, while in the winter it belongs to a less continental climate.

The following diagram (fig. 4) gives the daily means of temperature in Nertchinsk for the months of May and June.

Fig. 4.



The diagram shows that the increase of temperature proceeds by steps. Going up the curve slides down here and there and goes up again. The total depression of the yearly amplitude, due to these steps, may be estimated at 17° . Admitting this estimate and supposing that a curve of

67° ($=50+17$) amplitude would represent the variation corresponding to the coefficient of perfect atmospheric transparency* at the latitude of Nertchinsk, the lowest temperature of January must be considered $6^{\circ}5$ too high, and the highest July temperature $11^{\circ}5$ too low, since the extreme daily mean temperatures should be -37° and $+30^{\circ}$.

Thus it may be that, in this case, the decrease in amplitude is in close connexion with the annual variation of atmospheric moisture. During the summer months, the greater amount of aqueous vapour diminishes the coefficient of atmospheric (thermal) transparency very much more than during the winter months, and so it is evident that the summer temperatures differ more from what they should be than the temperatures observed during the winter.

This leads to the question whether the steps of the Nertchinsk temperature curve, and perhaps also the steps of the curves of several other stations, are not partially due to a rhythmical transport of atmospheric moisture.

In the ascending part of the curve of Barnaoul the depressions following the crests generally precede by 2 to 4 days the corresponding details of the curve of Nertchinsk. The inflexions of the isotherms characteristic for these changes progress therefore across Siberia from the W. towards the E.

But, as a result of the International Balloon ascents of May 13th, 1897, Hergesell has shown that the typical decrease of temperature observed then in Central Europe was very much more accentuated at high altitudes than it was near the ground†. Similar observations have been made since. In consequence, the inflexion of the isotherms must be more pronounced at an altitude of 10,000 m. than it is at the surface of the earth's crust. After each step of the ascending temperature curve the entire air-mass above the station where the step has been observed is changed. The work of the progressive heating of the ground by solar radiation and the heating of the air-mass above by convection currents, must, to a certain extent, be begun anew, and probably under different conditions.

Evidently, to reach a definite conclusion it would be necessary to study the records of individual years and the weather maps as well. But the real difficulty, and at the same time the great interest of the study of these normal

* A. Angot, *Ann. Bur. Centr. Met. France*, vol. i. p. B. 121 (1883).

† *Meteor. Zeit.* vol. xvii. p. 1 (1900).

anomalies of the mean annual temperature variation, resides in the fact that we have to deal with a phenomenon showing intimate relationship between very far distant stations.

On the opposite side of the world, in Baltimore*, the temperature crests of February 22nd, March 10th, April 14th, and May 10th, there observed, belong also to the curves of Barnaoul and Nertchinsk. In Barnaoul they occur: February 18, March 9, April 21, and May 10. In Nertchinsk, February 22, March 12, April 20 (and May 12).

Already Dove† noticed the fact that the anomaly occurring during the month of May is noticeable in the records collected in Arctic America and Greenland. On the other hand, according to R. C. Mossman‡, the cold period of May is well pronounced in Argentina and Chile, north of 40° S. lat., and it was also observed at the winter quarters of the 'Discovery' in 1902 and 1903, at Cape Adare in 1899, at the South Orkneys during all the years of observation from 1903 to 1908, with the exception of 1906.

Mossman remarks that thus the temperature anomaly of May is a bipolar phenomenon, and he adds that the curve of mean atmospheric pressure at the South Orkneys, for each day of the year, bears a close resemblance to that of Edinburgh.

Forcibly therefore we reach the conclusion that in a comparative study of the anomalies of the annual temperature variation, Teisserene de Bort's conception of the great centres of action of atmospheric circulation will find an extensive application; because, although at present it would be premature to try to explain why it is that some changes of phase may occur simultaneously in Arctic and Antarctic regions, or in North America and Siberia, it seems impossible to conceive such correlations without supposing some relationship with the exchange of pressure between the seasonal and permanent centres of action.

New York City, November 2, 1916.

* O. L. Fassig, 'The Climate and Weather of Baltimore,' pl. 3, Baltimore, 1907.

† *Loc. cit.*

‡ Symon's Met. Mag. vol. xliv. p. 1 (1909).

XLVII. *The Theory of Anomalous Dispersion.*

By Lord RAYLEIGH, O.M., F.R.S.*

IN a short note † with the above title I pointed out that Maxwell as early as 1869 in a published examination paper had given the appropriate formulæ, thus anticipating the work of Sellmeier ‡ and Helmholtz §. It will easily be understood that the German writers were unacquainted with Maxwell's formulæ, which indeed seem to have been little known even in England. I have thought that it would be of more than historical interest to examine the relation between Maxwell's and Helmholtz's work. It appears that the generalization attempted by the latter is nugatory, unless we are prepared to accept a refractive index in the dispersive medium becoming infinite with the wave-length in vacuo.

In the æther the equation of plane waves propagated in the direction of x is in Maxwell's notation

$$\rho d^2\eta/dt^2 = E d^2\eta/dx^2, \quad . \quad . \quad . \quad . \quad (1)$$

where η is the transverse displacement at any point x and time t , ρ is the density and E the coefficient of elasticity. Maxwell supposes "that every part of this medium is connected with an atom of other matter by an attractive force varying as distance, and that there is also a force of resistance between the medium and the atoms varying as their relative velocity, the atoms being independent of each other"; and he shows that the equations of propagation in this compound medium are

$$\rho \frac{d^2\eta}{dt^2} - E \frac{d^2\eta}{dx^2} = \sigma \left(p^2 \zeta + R \frac{d\zeta}{dt} \right) = -\sigma \left(\frac{d^2\eta}{dt^2} + \frac{d^2\zeta}{dt^2} \right), \quad (2)$$

where ρ and σ are the quantities of the medium and of the atoms respectively in unit of volume, η is the displacement of the medium, and $\eta + \zeta$ that of the atoms, $\sigma p^2 \zeta$ is the attraction, and $\sigma R d\zeta/dt$ is the resistance to the relative motion per unit of volume.

* Communicated by the Author.

† Phil. Mag. vol. xlviii. p. 151 (1899); Scientific Papers, vol. iv. p. 413. A misprint is now corrected, see (4) below.

‡ Pogg. Ann. cxliii. p. 272 (1871).

§ Pogg. Ann. cliv. p. 582 (1874).

On the assumption that

$$\eta, \zeta = (C, D) e^{int} e^{-(1/l + in/v)x},$$

we get Maxwell's results *

$$\frac{1}{v^2} - \frac{1}{l^2 n^2} = \frac{\rho + \sigma}{E} + \frac{\sigma n^2}{E} \frac{p^2 - n^2}{(p^2 - n^2)^2 + R^2 n^2}, \quad \dots \quad (4)$$

$$\frac{2}{v l n} = \frac{\sigma n^2}{E} \frac{R n}{(p^2 - n^2)^2 + R^2 n^2}. \quad \dots \quad (5)$$

Here v is the velocity of propagation of phase, and l is the distance the waves must run in order that the amplitude of vibration may be reduced in the ratio $e : 1$.

When we suppose that $R = 0$, and consequently that $l = \infty$, (4) simplifies. If v_0 be the velocity in æther ($\sigma = 0$), and ν be the refractive index,

$$\nu^2 = \frac{v_0^2}{v^2} = 1 + \frac{\sigma}{\rho} \frac{p^2}{p^2 - n^2}. \quad \dots \quad (6)$$

For comparison with experiment, results are often conveniently expressed in terms of the wave-lengths in free æther corresponding with the frequencies in question. Thus, if λ correspond with n and Λ with p , (6) may be written

$$\nu^2 = 1 + \frac{\sigma}{\rho} \frac{\lambda^2}{\lambda^2 - \Lambda^2}, \quad \dots \quad (7)$$

—the dispersion formula commonly named after Sellmeier. It will be observed that p, Λ refer to the vibrations which the atoms might freely execute when the æther is maintained at rest ($\eta = 0$).

If we suppose that n is infinitely small, or λ infinitely great,

$$\nu_\infty^2 = 1 + \sigma/\rho, \quad \dots \quad (8)$$

thus remaining finite.

Helmholtz in his investigation also introduces a dissipative force, as is necessary to avoid infinities when $n = p$, but one differing from Maxwell's, in that it is dependent upon the absolute velocity of the atoms instead of upon the *relative*

* Thus in Maxwell's original statement. In my quotation of 1899 the sign of the second term in (4) was erroneously given as *plus*.

velocity of æther and matter. A more important difference is the introduction of an additional force of restitution (a^2x), proportional to the absolute displacement of the atoms. His equations are

$$\mu \frac{d^2\xi}{dt^2} = \alpha^2 \frac{d^2\xi}{dy^2} + \beta^2(x - \xi), \quad (9) *$$

$$m \frac{d^2x}{dt^2} = \beta^2(\xi - x) - \alpha^2x - \gamma^2 \frac{dx}{dt}. \quad (10)$$

This notation is so different from Maxwell's, that it may be well to exhibit explicitly the correspondence of symbols.

| | | | | | | | | | | |
|-----------------|--------|--------|------------|-----|-----------|--------------|----------|-------|-----|-------|
| Helmholtz . . | ξ | μ | α^2 | y | $x - \xi$ | β^2 | m | a^2 | c | k |
| Maxwell | η | ρ | E | x | ζ | σp^2 | σ | 0 | v | $1/l$ |

When there is no dissipation ($R=0$, $\gamma^2=0$), these interchanges harmonize the two pairs of equations. The terms involving respectively R and γ^2 follow different laws.

Similarly Helmholtz's results

$$\frac{1}{c^2} - \frac{k^2}{n^2} = \frac{\mu}{\alpha^2} - \frac{\beta^2}{\alpha^2 n^2} - \frac{\beta^4}{\alpha^2 n^2} \frac{mn^2 - a^2 - \beta^2}{(mn^2 - a^2 - \beta^2)^2 + \gamma^4 n^2}, \quad (11)$$

$$\frac{2k}{cn} = - \frac{\beta^4 \gamma^2}{\alpha^2 n} \frac{1}{(mn^2 - a^2 - \beta^2)^2 + \gamma^4 n^2}, \quad (12)$$

identify themselves with Maxwell's, when we omit R and γ^2 and make $a^2=0$.

In order to examine the effect of a^2 , we see that when $\gamma=0$, (11) becomes

$$\frac{1}{c^2} = \frac{\mu}{\alpha^2} - \frac{\beta^2}{\alpha^2 n^2} \frac{mn^2 - a^2}{mn^2 - a^2 - \beta^2}, \quad (13)$$

or in terms of $\nu^2 (=c_0^2/c^2)$,

$$\nu^2 = 1 - \frac{\beta^2}{\mu} \frac{m - a^2/n^2}{mn^2 - a^2 - \beta^2}. \quad (14)$$

If now in (14) we suppose $n=0$, or $\lambda=\infty$, we find that $\nu=0$, unless $a^2=0$. If $a^2=0$, we get, in harmony with (6),

$$\nu^2 = 1 - \frac{m\beta^2}{\mu(mn^2 - \beta^2)}, \quad (15)$$

* What was doubtless meant to be $d^2\xi/dy^2$ appears as $d^2\xi/dx^2$, bringing in x in two senses.

which is finite, unless $mn^2 = \beta^2$. It is singular that Helmholtz makes precisely opposite statements:—"Wenn $a=0$, wird $k=0$ and $1/c=\infty$; sonst werden beide Werthe endlich sein."

The same conclusion may be deduced immediately from the original equations (9), (10). For if the frequency be zero and the velocity of propagation in the medium finite, all the differential coefficients may be omitted; so that (9) requires $x-\xi=0$ and (10) then gives $a^2=0$.

Wüllner*, retaining a^2 in Helmholtz's equation, writes (14) in the form

$$\nu^2 = 1 - P\lambda^2 + \frac{Q\lambda^4}{\lambda^2 - \Lambda^2}, \quad . \quad . \quad . \quad (16)$$

applicable when there is no absorption. And he finds that in many cases the facts of observation require us to suppose $P=Q$. This is obviously the condition that ν^2 shall remain finite when $\lambda=\infty$, and it requires that a^2 in Helmholtz's equation be zero. It is true that in some cases a better agreement with observation may be obtained by allowing Q to differ slightly from P , but this circumstance is of little significance. The introduction of a new arbitrary constant into an empirical formula will naturally effect some improvement over a limited range.

It remains to consider whether *a priori* we have grounds for the assumption that ν is finite when $\lambda=\infty$. On the electromagnetic theory this should certainly be the case. Moreover, an infinite refractive index must entail *complete* reflexion when radiation falls upon the substance, even at perpendicular incidence. So far as observation goes, there is no reason for thinking that dark heat is so reflected. It would seem then that the introduction of a^2 is a step in the wrong direction and that Helmholtz's formulæ are no improvement upon Maxwell's.

It is scarcely necessary to add that the full development of these ideas requires the recognition of more than one resonance as admissible (Sellmeier).

* Wied. *Ann.* xvii. p. 580; xxiii. p. 306.

XLVIII. *Adiabatic Invariants and the Theory of Quanta.*

By P. EHRENFEST *.

CONTENTS:—(1) Definition of a reversible adiabatic transformation of a mechanical system. Systems which are *adiabatically related* to each other.—(2) Formulation of an hypothesis on adiabatic transformations for systems with periodic or quasi-periodic motions.—(3) Adiabatic Invariants and their use.—(4) The adiabatic invariant $\frac{2T}{\nu}$ for periodic motions, and $\frac{\epsilon}{\nu}$ especially for harmonic motions.—(5) Geometrical interpretation of the adiabatic invariant $\frac{2T}{\nu}$ in the phase-space.—(6) Connexion with the formulæ of the Theory of Quanta, as proposed by Planck, Debye and others for systems of one degree of freedom.—(7) Connexion with Sommerfeld's formulæ for systems of more degrees of freedom.—(8) Connexion with the statistical roots of the Second Law of Thermodynamics.—(9) Difficulties which arise by a passage through singular motions. Aperiodical motions.—(10) Conclusion.

Introduction.

In the treatment of a continually increasing number of physical problems, use is at the same time made of the principles of classical mechanics and electrodynamics, and of the hypothesis of the quanta, which is in conflict with them. Through the study of these problems it is hoped to arrive at some general point of view which may trace the boundary between the "classical region" and the "region of the quanta."

One fundamental law stands amidst the theory of quanta, which is wholly derived from classical foundations: the *Displacement Law* of W. Wien on the change of the distribution of energy over the spectrum involved by a reversible adiabatic compression of radiation. This fact deserves our attention. It might be possible that also in more general cases, when we do not restrict ourselves to harmonic motions, the reversible adiabatic transformations should be treated in a classical way, whereas in the calculation of other processes (*e. g.* an isothermal addition of heat) the quanta come into play.

From this point of view I started in some papers in which on the one hand I studied Planck's hypothesis of energy elements †, and on the other tried to extend this hypothesis

* Communicated by the Author. Abridged translation of a paper published in the Proc. Acad. of Amsterdam, xxv. (1916) p. 412.

† P. Ehrenfest, *Ann. d. Phys.* vol. xxxvi. (1911) pp. 91–118 (quoted as paper A).

- (2) To demonstrate the importance of the “*adiabatic invariants*” for the theory of quanta. In this respect the discussion of the invariant $\frac{2T}{\nu}$ mentioned above gives the connexion between the adiabatic hypothesis and the formulæ by which Planck, Debye, Bohr, Sommerfeld and others have introduced the quanta.
- (3) To indicate the difficulties which arise in the application of the hypothesis, if the reversible adiabatic transformation leads through singular motions.
- (4) To indicate the connexion between the adiabatic problems and the statistical-mechanical roots of the Second Law of Thermodynamics. Boltzmann’s deduction of this law is based upon a statistical principle which has been destroyed by the introduction of the quanta. At the present time we possess a statistical deduction of this law for some special systems (*e. g.* for systems with simple harmonic motions) but not for general systems*.

I take the liberty of publishing my considerations, in the hope that others may overcome the difficulties which I could not solve. Perhaps on closer examination it will appear that the adiabatic hypothesis is not generally valid; in any case, the correctness of Wien’s displacement law seems to indicate that the reversible adiabatic processes take a prominent place in the theory of quanta—it seems that they may be treated in a “classical” way.

§ 1. *Definition of a reversible adiabatic affection of a system. Motions $\beta(a)$ and $\beta(a')$ which are adiabatically related to each other.*

Let the coordinates of the system be denoted by $q_1 \dots q_n$. The potential energy Φ may contain besides the coordinates q certain “parameters” $a_1, a_2 \dots$, the values of which can be altered infinitely slowly. The kinetic energy T may be a homogeneous quadratic function of the velocities $\dot{q}_1 \dots \dot{q}_n$, the coefficients of which are functions of the q and may be of the $a_1, a_2 \dots$. By changing the parameters from the values $a_1, a_2 \dots$ to the values $a'_1, a'_2 \dots$ in an infinitely slow way, a given motion $\beta(a)$ may be transformed into another motion $\beta(a')$. This special type of influencing upon the system may be called “a reversible adiabatic affection,” the motions $\beta(a)$ and $\beta(a')$ “adiabatically related to each other.”

* P. Ehrenfest, *Physik. Zeitschr.* vol. xv. (1914) p. 657 (paper D). Also § 8 of this paper.

Remarks.—A. If some of the motions considered are distinctly non-periodic (*e. g.* the hyperbolic motion in the case of a Newtonian attraction), the addition “reversible” loses its original meaning.

B. The definition given above must be generalized in a suitable manner, if the system is affected by an (infinitely slowly increasing) magnetic field (Zeeman effect), or if the mechanical system is replaced by an electrodynamical one (reversible adiabatic compression of radiation).

§ 2. *Formulation of the adiabatic hypothesis for systems with periodical or quasi-periodical motions.*

Consider the system first when the parameters have some given values $a_{10}, a_{20} \dots$. The theory of quanta will not allow every motion $\beta(a_0)$, which is possible with these values of the parameters according to the equations of the classical mechanics, but only some distinct special motions*. Consequently we speak of the “allowed” motions $B\{a_0\}$ belonging to the values $a_{10}, a_{20} \dots$ of the parameters. To any other values $a_1, a_2 \dots$ belong other “allowed” motions $B\{a\}$. Now our hypothesis asserts:

For general values $a_1, a_2 \dots$ of the parameters, those and only those motions are allowed which are adiabatically related to the motions which were allowed for the special values $a_{10}, a_{20} \dots$ (*i. e.* which can be transformed into them, or may be derived from them in an adiabatic reversible way).

Remarks.—A. Whether it be possible to extend the hypothesis to non-periodic motions, and how this should be done, I am not able to tell on account of some difficulties, which are mentioned in § 9.

B. Some forms of adiabatic affections may be realized physically—for instance, the strengthening of an electric or a magnetic field surrounding an atom (Stark and Zeeman effect). Others have more the character of a mathematical fiction (*e. g.* the change of a central field of force).

§ 3. *The Adiabatic Invariants and their application.*

Each application of the adiabatic hypothesis forces us to look for “adiabatic invariants”—that is, for quantities which

* In the newer form of his radiation theory, Planck speaks only of “critical” motions, besides which other motions are “allowed” too. In order not to become too diffuse, we will leave this form of the theory of quanta out of consideration. The suitable adaptation of the considerations given in this paper is easily to be found.

retain their value during the transformation of a motion $\beta(a)$ into a motion $\beta(a')$ related adiabatically to the former. Indeed, from the hypothesis follows immediately the property :

If an adiabatic invariant Ω for the "allowed" motions $B\{a_0\}$, belonging to the *special* values $a_{10}, a_{20} \dots$, possesses the distinct numerical values $\Omega', \Omega'' \dots$, it possesses *exactly the same values* for the "allowed" motions belonging to *arbitrary* values of the parameters $a_1, a_2 \dots$

§ 4. The adiabatic invariant $\frac{2T}{\nu}$ for periodic motions and $\frac{\epsilon}{\nu}$ especially for harmonic motions*.

Suppose that the system under consideration possesses the following properties:—For arbitrarily fixed values of the parameters $a_1, a_2 \dots$, all the motions that have to be considered are *periodic*, independently of the phases ($q_{10} \dots q_{n0}, \dot{q}_{10} \dots \dot{q}_{n0}$) the motion starts with. The period P may depend in some way or other on the $a_1, a_2 \dots$ and on the beginning phase.

Then the integral with respect to time of twice the kinetic energy, extended over one period, is an adiabatic invariant :

$$\delta' \int_0^P dt \cdot 2T = 0. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

In this formula δ' denotes the difference in value for two infinitely near, adiabatically related motions of the system. (For the demonstration of form. 3 the reader is referred to the original paper, Proc. Acad. Amsterdam, xxv. (1916) p. 412. Putting the reciprocal of the period P equal to the frequency ν , and denoting the mean of T with respect to the time by \bar{T} , form. 3 expresses :

$$\frac{2\bar{T}}{\nu} = \text{adiabatic invariant.} \quad . \quad . \quad . \quad (4)$$

* Comp. paper C, § 1, 2. *Other instances of adiabatic invariants:* If the system possesses cyclic coordinates, the cyclic momenta are invariants. If the rotation of a ring of electrons is affected by an increasing magnetic field, the *sum of the moment of momentum and of the electrokinetic moment* is an invariant (Zeeman effect, magnetization). If an increasing electric field acts on a hydrogen atom of Bohr, then the component of the moment of momentum parallel to the lines of force is an invariant. For changes of a central field of force it is the moment of momentum.

In the case of a simple harmonic motion of one degree of freedom we know that the mean of the kinetic energy is equal to the mean of the potential energy; hence both of them are equal to half the total energy. So here we have

$$\frac{\epsilon}{\nu} = \text{adiabatic invariant} \dots \dots \dots (5)$$

§ 5. Geometrical interpretation of the adiabatic invariant $\frac{2T}{\nu}$ in the phase-space (q - p space).

To get a connexion with the formulæ used by Planck, Debye, Bohr, Sommerfeld and others to introduce the quanta, we will avail ourselves of a transformation of the *integral of Action*, to which Sommerfeld has drawn attention*:

$$\int_0^P dt \cdot 2T = \int_0^P dt \sum_h p_h \dot{q}_h = \sum_h \int dq_h \cdot p_h = \sum_h \iint dp_h dq_h \dots \dots (6)$$

Hence

$$\frac{2T}{\nu} = \sum_h \iint dp_h dq_h \dots \dots \dots (7)$$

The double integrations at the right-hand side have the following meaning: When the system performs its periodic motion, its phase-point describes a closed curve† in the $2n$ -dimensional q - p space, and its n projections on the two-dimensional surfaces (q_1, p_1) , $(q_2, p_2) \dots (q_n, p_n)$ describe n closed curves. $\iint dp_h dq_h$ is the area of the region enclosed by the h^{th} projection curve.

Remarks.—A. The numerical value of $\frac{2T}{\nu}$ is not changed if we pass to another system of coordinates for the description of the motion. Hence also the numerical value of the right-hand side of equation (7) is independent of the system of coordinates used.

B. Systems exist possessing the following property: with a *suitable choice of the system of coordinates* not only is the total sum at the right-hand side of (7) an adiabatic invariant, but *each separate integral* $\iint dp_h dq_h$ is an invariant. Compare the example of § 7.

* A. Sommerfeld, *Sitzungsber. d. bayr. Akad.* 1916, pp. 425–500 (§ 7).

† This expression must be altered in some way, if any of the coordinates be angles which increase by 2π in each period.

C. For systems of one degree of freedom we have according to (7) :

$$\frac{\overline{2T}}{\nu} = \iint dq dp = \text{adiabatic invariant.} \quad \dots \quad (8)$$

i. e. for systems of one degree of freedom the area enclosed by the phase-curve in the q - p diagram is an invariant (in this case there exists no other invariant which is independent of the former).

D. A theorem by P. Hertz (1910) *. Imagine a system of n degrees of freedom and consider any motion belonging to a set of given values $a_{10}, a_{20} \dots$ of the parameters. The corresponding phase-curve in the $2n$ -dimensional q - p space lies wholly on a certain hypersurface of constant energy, $\epsilon(q, p, a_0) = \epsilon_0$, which encloses a certain $2n$ -dimensional volume :

$$V_0 = \int \dots \int dq \dots dq_n \dots \dots \dots (9)$$

An adiabatic reversible affection $a_0 \rightarrow a_1$: firstly, changes the value of the energy (by the amount of the work performed on the system) ; secondly, alters the form and position of the hypersurfaces $\epsilon(q, p, a) = \text{const.}$ Let the volume enclosed by that surface of constant energy on which lies the phase-curve of the system after the affection be V . Then the theorem of P. Hertz asserts that

$$V = V_0 \dots \dots \dots (10)$$

For systems of one degree of freedom (10) and (8) coincide, for more degrees of freedom this is not the case.

§ 6. *Connexion with the formulæ of the Theory of Quanta, as proposed by Planck, Debye and others for systems of one degree of freedom.*

Planck's hypothesis of energy elements (1901) asserts that an harmonically vibrating resonator of frequency ν_0 can contain only the following amounts of energy† :

$$\epsilon = 0, h\nu_0, 2h\nu_0 \dots \dots \dots (11)$$

Hence the adiabatic invariant of the resonator may take only the values :

$$\frac{\epsilon}{\nu_0} = \frac{\overline{2T}}{\nu_0} = \iint dq dp = 0, h, 2h \dots \dots (12)$$

Let us consider a resonator with a non-linear equation of motion :

$$\ddot{q} = -(\nu_0^2 q + a_1 q^2 + a_2 q^3 \dots) \dots \dots (13)$$

* P. Hertz, *Ann. d. Phys.* vol. xxxiii. (1910) pp. 225, 537, § 11.

† Comp. note *, § 2, p. 503.

Its vibrations are not harmonical, and the frequency $\nu \neq \nu_0$ does not depend only on the values of the parameters a_1, a_2, \dots , but also on the exciting force. For the special values of the parameters

$$a_1 = a_2 = \dots = 0,$$

it passes into Planck's resonator. Hence from the adiabatic hypothesis (comp. the formulation in § 3) follows: also for non-harmonically vibrating resonators only those motions are allowed for which

$$\frac{2\bar{T}}{\nu} = \iint dq dp = 0, h, 2h, \dots \quad (14)$$

So by means of the adiabatic hypothesis we have derived Debye's hypothesis on the values of $\iint dq dp$ for non-harmonical vibrations* from Planck's hypothesis of energy elements.

An electrical doublet with the electrical moment a_1 , the moment of inertia a_2 , is suspended in such a way that it can turn freely about the z axis†. An electrical field of intensity a_3 acts parallel to the axis of x . As the coordinate q we choose the position-angle of the doublet. We will begin with very great values of a_1, a_3 , and also of a_2 ; then even for great values of the exciting energy we may consider the vibrations as infinitely small and harmonical—resonator of Planck's type. By diminishing infinitely slowly the values of a_2 and a_3 we can pass in a reversible adiabatic way to vibrations of finite amplitude, and then make the pendulum "turn over"; if now the moment of inertia a_2 is no more changed, but the directing field a_3 is diminished to zero, we arrive at a molecule which *rotates uniformly, uninfluenced by any force*. For all the motions considered, which are related adiabatically to each other, the adiabatic invariant

$$\frac{2\bar{T}}{\nu} = \iint dq dp$$

has to retain its original values $0, h, 2h, \dots$. If for the uniform rotation we identify the frequency ν with the number of rotations of the doublet in unit of time

$$\nu = \pm \dot{q}/2\pi, \quad \dots \quad (15)$$

and observe that

$$2\bar{T} = 2T = p\dot{q}, \quad \dots \quad (16)$$

* P. Debye, *Quantenhypothese* (Göttinger Vorl. Teubner, 1913). Comp. also S. Boguslawski, *Physik. Zeitschr.* xv. (1914) p. 569.

† Comp. the treatment and the use of this example in papers B and C. Comp. especially the diagram given in C, § 3.

we must demand that p can take no other values than

$$p=0, \quad \pm \frac{h}{2\pi}, \quad \pm 2 \cdot \frac{h}{2\pi} \cdot \quad . \quad . \quad . \quad (17)$$

Remark.—The discussion sketched in the preceding lines wants to be developed more sharply, as the adiabatic transformation passes through a singular unperiodical motion, which forms the limit between the oscillatory and the rotatory motions. It is necessary to analyse more precisely the connexion between the adiabatic invariants for both types of motion.

§ 7. *Connexion with Sommerfeld's formulæ for systems of more than one degree of freedom.*

We will show that the quantum formulæ, which Sommerfeld has given for the motion of a point in a plane about a Newtonian centre of attraction, satisfy the adiabatic hypothesis.

Let $\chi(r, a_1, a_2 \dots)$ be the potential of a central attractive force. The differential equations of the plane motion of a point, written in polar coordinates, have the form

$$m\ddot{r} - mr\dot{\phi}^2 + \frac{d\chi}{dr} = 0, \quad . \quad . \quad . \quad (18a)$$

$$\frac{d}{dt}(mr^2\dot{\phi}) = 0. \quad . \quad . \quad . \quad (18b)$$

From (18b) we see immediately that the moment of momentum is an invariant against a change of the parameters $a_1, a_2 \dots$

$$mr^2\dot{\phi} = p_2 = \text{adiabatic invariant} \quad . \quad (19)$$

Eliminating $\dot{\phi}$ from eq. (18a) with the aid of (19), we get

$$m\ddot{r} = \frac{p_2^2}{mr^3} - \frac{d\chi}{dr} \quad . \quad . \quad . \quad (20)$$

This equation has the same structure as the differential equation for the motion of a point, which oscillates along a straight line under the influence of a potential

$$\Phi = + \frac{p_2^2}{2mr^2} + \chi(r, a_1, a_2) \quad . \quad . \quad (21)$$

between two limiting values of r ($r_A > r_B > 0$). But, according to §§ 4 and 5, this periodical motion of one degree of freedom possesses the adiabatic invariant

$$\frac{2T_1}{\nu_1} = \iint dq_1 dp_1 = \text{adiabatic invariant} \quad (22)$$

Note that also eq. (19) may be written in the same form :

$$\frac{2\overline{T_2}}{\nu_2} = \iint dq_2 dp_2 = \text{adiabatic invariant.} \quad (23)$$

For we have

$$\frac{2\overline{T_2}}{\nu_2} = \frac{p_2 \dot{q}_2}{\left(\frac{\dot{q}_2}{2\pi}\right)} = 2\pi p_2 = \int_0^{2\pi} dq_2 \cdot p_2 = \iint dq_2 dp_2.$$

Now Sommerfeld's formulæ are *

$$\iint dq_1 dp_1 = 0, h, 2h \dots nh. \quad . \quad . \quad . \quad . \quad . \quad (24)$$

$$\iint dq_2 dp_2 = 0, h \dots n'h. \quad . \quad . \quad . \quad . \quad . \quad (25)$$

So they satisfy the adiabatic hypothesis (comp. its form in § 3).

Remarks.—A. We have seen that the adiabatic invariants (22) and (23) exist not only for periodic motions about a Newtonian or about a quasi-elastic centre of force, but also for the quasi-periodic motions with a more general $\chi(r, a)$. Only in the former case $\nu_1 = \nu_2 = \nu$; so there we may combine the two invariants into the one

$$\frac{2(\overline{T_1 + T_2})}{\nu} = \frac{2\overline{T}}{\nu} = \text{adiabatic invariant.}$$

B. It would be of great interest to find the adiabatic invariants for more general quasi-periodic motions, and especially for anisotropic fields of force, instead of the isotropic fields, which are treated above. Then at the same time we should understand better which system of coordinates should be used for the application of Sommerfeld's formulæ †.

§ 8. *Connexion with the statistical roots of the Second Law of Thermodynamics* ‡.

In his statistical mechanical deduction of the Second Law of Thermodynamics, and especially of the equation

$$\frac{\Delta E + A_1 \Delta a_1 + A_2 \Delta a_2 \dots}{\Theta} = k \Delta \log W, \quad . \quad (26)$$

Boltzmann based himself upon a certain supposition on the “probability a priori” of regions in the q - p space of the molecules (μ space); he considered those regions as “a priori equally probable” which correspond with equal volumes $\int \dots \int dq_1 \dots dp_n$ in the μ space. In other words, Boltzmann gave the μ space everywhere the same “weight”

$$G(q, p) = \text{const.} \quad . \quad . \quad . \quad . \quad . \quad (27)$$

* A. Sommerfeld, *Sitzungsber. d. bayr. Akad.* 1916, pp. 425–500.

† A. Sommerfeld, *l. c.* p. 455 at the foot.

‡ Cf. P. Ehrenfest, *Phys. Zeitschr.* xv. (1914), p. 657 (paper D).

Planck's hypothesis of energy elements and its generalizations destroy this basis; they introduce, as it may be expressed, a weight depending on q, p , and a

$$G(q, p, a); \dots \dots \dots (28)$$

all regions of the μ space have the "*weight zero*" (are "*forbidden*") with the exception of the discontinuously distributed "*allowed*" regions, the position of which depends on the value of the parameters a^* . The latter circumstance is of particular importance.

So we arrive at the following problem: In what manner must the choice of the "*weight-function*" $G(q, p, a)$ —in other words, the choice of the "*allowed*" regions—be limited, especially in their dependence on the a , in order that Boltzmann's equation (26) may remain valid?

I have treated this problem first in a special case †, then generally ‡.

For molecules of one degree of freedom (harmonically and unharmonically vibrating resonators) I could wholly solve the question. The result I arrived at § may be expressed in the language of this article in the following form:

An ensemble of such-like molecules (resonators) will fulfil Boltzmann's relation between entropy and probability if, and only if, the allowed motions are determined by means of the adiabatically invariant condition

$$\frac{2T}{\nu} = \iint dq dp = \text{fixed numerical values } \Omega_1, \Omega_2, \dots \quad (29) \parallel$$

Planck's hypothesis on the elements of energy for harmonically vibrating oscillators and its generalization by Debye satisfy this condition; in this case $\Omega_1, \Omega_2, \dots$ are taken equal to $0, h, 2h, \dots$ ¶ (comp. § 5, equation (14).

* The form and dimensions of the "*allowed*" ellipses in the q - p diagram of a Planck's resonator are altered if the inertia and elasticity of the resonator are changed. In an analogous way the "*allowed*" ellipses, belonging to the principal modes of vibration of a "*Hohlraum*" or of the lattice of a crystal, are altered by a compression.

† Paper A, § 5.

‡ Paper D.

§ Paper D, § 7, remark.

¶ *L. c.* § 7, this invariant is noted by i .

¶ That Planck's hypothesis on the energy elements is in harmony with the Second Law (and with the adiabatic hypothesis) has come about in the following way: in the deduction of his theory of radiation Planck at a certain moment puts the elements of energy (which were not yet determined before) equal to $h\nu$ in order to make his radiation formula correspond with the displacement law of W. Wien (*cf.* Planck, *Vorlesungen über Wärmestrahlung*, 1st edition, 1906, p. 153, eq. 226). Compare also the other quantum formulæ, paper D, § 6.

As yet I have not been able to tell if also for molecules of *more than one* degree of freedom the same *necessary* and *sufficient* relations hold between the *adiabatic invariants* on the one hand and the *fulfilment of Boltzmann's theorem* on the other.

Remarks.—A. In recent years it has become usual to introduce the relations between probability and entropy (or free energy)

$$S = k \log W \quad . \quad . \quad . \quad . \quad . \quad . \quad (30)$$

$$F = E - T k \log W \quad . \quad . \quad . \quad . \quad . \quad . \quad (31)$$

simply as a *postulate*. It might seem that in this case the problem discussed in this paragraph becomes superfluous. However, this method of treating only shifts the difficulty to another point, as I have shown*.

B†. A reversible adiabatic compression transforms black body radiation into black body radiation, by which process it is immaterial if a little piece of a black body is present to act as a “catalyzator” or not. Similarly Maxwell’s velocity distribution in a gas consisting of point molecules which exert no forces on each other is transformed into a velocity distribution of the same kind by a reversible adiabatic compression of the gas (in a rough-walled vessel), independently of the occurrence of collisions between the molecules‡. Hence we may ask more generally: Does a *most probable* distribution of states in an ensemble of molecules (resonators) pass always into a *most probable* distribution when the ensemble is subjected to an adiabatic reversible affection independently of the occurrence of interaction between the molecules during the affection? With the exception of special cases, this question must be answered in the negative §.

* Paper D, Introduction.

† Cf. paper C, § 4.

‡ Both examples have the following property in common: The pressure depends only on the *total energy* of the system, it is independent of the distribution of the energy over the different principal modes of vibration or over the molecules. In the cycle compression, catalytic process, dilatation, adiabatic process, the same amount of work is given to the system as is taken from it. For general systems this is no longer the case.

§ Without any calculation this may be shown by means of the following example:—Imagine an ideal gas with rigid ellipsoidal molecules; the walls of the vessel are replaced by a field of force which reflects only the centre of gravity of the molecules (the reflexion is perfectly elastic); if the gas is compressed adiabatically, without collisions between the molecules taking place, the kinetic energy of the translatory motion is increased, but not the energy of the rotatory motion. If collisions between the molecules do take place, this is otherwise. By a short calculation it may be shown by the following example:—Point molecules move up and down along a straight line between two fixed points A and B, uninfluenced by any force. An elastic field of force is excited infinitely slowly, so that in the end the molecules perform harmonic vibrations about the centre of the line.

§ 9. *Difficulties which arise by a passage through singular motions. Aperiodic motions.*

One of these difficulties has already been mentioned at the end of § 6. A difficulty of a slightly different form arises when we pass in an adiabatic reversible way from the vibrations in an anisotropic quasi-elastic field of force to those in an isotropic field *. If we begin with an anisotropic field, with potential energy

$$\Phi = \frac{1}{2} (\nu_1^2 \xi_1^2 + \nu_2^2 \xi_2^2) \dagger, \quad . \quad . \quad . \quad (32)$$

it is usual to treat each of the two principal modes of vibration according to Planck's method; only those motions are allowed for which the energies of the principal modes of vibration satisfy the equations

$$\frac{\epsilon_1}{\nu_1} = n_1 h; \quad \frac{\epsilon_2}{\nu_2} = n_2 h. \quad . \quad . \quad . \quad (33)$$

According to our hypothesis these equations must remain unchanged if ν_1 and ν_2 converge infinitely slowly to the same value. The field becomes isotropic, and the total energy satisfies the equation

$$\frac{\epsilon}{\nu} = (n_1 + n_2) h. \quad . \quad . \quad . \quad (34)$$

At the other hand, an isotropic field of force is a *central* field, hence Sommerfeld's formulæ can be applied here. These give:

$$\text{Moment of momentum} = m r^2 \dot{\phi} = n \frac{h}{2\pi}, \quad . \quad . \quad (35a)$$

$$\text{Total energy} = \epsilon = (n + n') h \nu. \quad . \quad . \quad (35b)$$

The motions allowed according to both sets of conditions are *not the same*; in the first place, we cannot see why the moment of momentum (which is not a constant in the anisotropic case, but oscillates between the values $\pm 2 \sqrt{n_1 n_2} \cdot h$) should converge to one of the distinct values given by (35a) for the isotropic case. These oscillations become slower and slower if ν_1 and ν_2 become more and more equal to each other, hence which value is attained when we have arrived at the isotropic case depends on a *double limiting process*. A second discrepancy, to which Epstein has drawn my attention, is the following: for a circular motion we must have in equation (35b) $n' = 0$, in (34), however, $n_1 = n_2$, hence in the latter case $\frac{\epsilon}{\nu}$ can be equal only to *even multiples*

* Comp. a remark made by H. A. Lorentz, Proc. Acad. Amsterdam (1912).

† The mass of the moving particle is supposed to be unity.

of h , whereas in the former it can be equal to *every integral multiple of h* .

From these considerations it appears that the adiabatic hypothesis wants a special complement in order that in this case (and also in the analogous cases of a passage through singular motions) the double limiting process should lead to a definite value. If such a complement could be found, it would be possible to deduce the quantum formulæ for arbitrary central forces from the hypothesis of energy elements for harmonically vibrating resonators.

At this place we must also mention the difficulties which arise if we try to extend the notions of "reversible adiabatic affection," "adiabatic invariant," &c., to families of motions which are essentially *unperiodic*—as, for instance, the hyperbolic motions of a point in a Newtonian field of force. In this case, too, the change of the energy and of the moment of momentum of the motion depend on a double limiting process: the course of the whole motion from $t = -\infty$ to $t = +\infty$, and the infinitely slow change of the parameters a_1, a_2, \dots .

§ 10. Conclusion.

The problems discussed in this paper show, as I hope, that the adiabatic hypothesis and the notion of adiabatic invariants are of importance for the extension of the theory of quanta to still more general classes of motions (§§ 6, 7); furthermore, that they throw some light on the question: What conditions are necessary that Boltzmann's relation between probability and entropy may remain valid (§ 8)?

Hence it would be of great interest to develop a systematic method of finding adiabatic invariants for systems as generally as possible.

The difficulties which arise by the passage through singular motions are yet awaiting their solution; perhaps it will be necessary to seek for some complement of the adiabatic hypothesis. In any case, it seems to me that the validity of Wien's displacement law shows that *reversible adiabatic affections take a prominent place in the theory of quanta*.

Postscriptum.—The beautiful researches of Epstein (*Ann. d. Phys.* l. pp. 489 & 815, 1916), Schwarzschild (*Sitzungsber. Berl. Akad.* 1916, p. 548), and others which have appeared in the meantime, show the great importance the cases which are integrable by means of Stäckel's method of "separation of the variables" have for the development of the theory of quanta. Hence the question arises: How far are the different parts into which these authors separate the integral of action according to Stäckel's method adiabatic invariants? In the problem treated by Sommerfeld this is the case, as is shown in § 7.

XLIX. *Adiabatic Invariants of Mechanical Systems* *.

By J. M. BURGERS †.

Introduction.

IN the course of the past year the Theory of Quanta has made great progress through the study of the so-called “*conditionally periodical*” systems ‡. The characteristic feature of these systems is that the integral of *Action*

$$W = \int 2T \cdot dt$$

(T = kinetic energy) can be separated into a sum of integrals, each of which depends on one only of the coordinates :

$$W = \sum_k \oint dq_k \sqrt{F_k(q_k)} \quad . \quad . \quad . \quad (1)$$

Generally the motion of each coordinate is a “*Libration*” : it goes up and down between two fixed limits, the values of which are determined by the integrated equations of motion §. For these systems the principle which is used to introduce the quantum of action h has the form

$$I_k = 2 \oint dq_k \sqrt{F_k(q_k)} = n_k \cdot h \quad . \quad . \quad . \quad (2)$$

(n_k denotes an integral number)

(during the integration q_k goes up and down once between its limits).

Now it has been shown by P. Ehrenfest || that for the theory of quanta the “*adiabatic invariants*” are of great importance. These quantities are functions belonging to the system, which have the property that their value is not changed when the system is disturbed adiabatically (see the precise definition by Ehrenfest, *l. c.* and below, § 1). Especially he has shown that in the older forms of the

* This article, Supplement No. 41c–41e of the Communications of the Physical Laboratory at Leiden, appeared for the first time in the Proc. Acad. of Amsterdam, xxv. (1916), pp. 849, 918, 1055. For those calculations which are treated only very shortly here the reader may be referred to the original paper.

† Communicated by Prof. H. Kamerlingh Onnes.

‡ K. Schwarzschild, *Sitz.-Ber. Berl. Akad.* 1916, p. 548.

P. Epstein, *Ann. d. Phys.* vol. I. (1916) p. 490; li. (1916) p. 168.

P. Debye, *Gött. Nachr.* 1916, p. 142; *Phys. Zeitschr.* xvii. (1916) pp. 507, 512.

A. Sommerfeld, *Phys. Zeitschr.* xvii. (1916) p. 491.

A general class of these systems was considered for the first time by P. Stäckel (*Comptes Rendus*, cxvi. (1898) p. 485; cxxi. (1895) p. 489). For an account of the theory, see C. L. Charlier, *Die Mechanik d. Himmels*, i. Leipzig, 1902.

§ Cf. Charlier, *l. c.* Compare also note * § 1 (p. 515).

|| P. Ehrenfest, *supra*, p. 500.

quantum-hypothesis, as used by Planck, Debye, Bohr, and Sommerfeld, the quantity which is put equal to an integral multiple of h is always an adiabatic invariant. As has already been remarked by Ehrenfest, it would be of great interest if this could be proved to be the case with the I_k mentioned above. In this paper it will be shown that, if we leave aside some special cases of degeneration, the I_k are really adiabatic invariants.

1. General considerations on Adiabatic Disturbances of a Mechanical System.

We will consider a mechanical system of n degrees of freedom; the coordinates are denoted by $q_1 \dots q_n$; the momenta by $p_1 \dots p_n$; the Hamiltonian function may be $H(q, p, a)$. We will suppose that none of the coordinates or of the momenta can increase indefinitely, and that the coordinates move between fixed limits*. (Supposition A.)

H does not depend only on q and p , but also on certain parameters a , e. g. masses, electric charges, intensity of an electric field, &c. Now during the motion of the system these parameters may be changed by influences from without. Such a variation of the parameters will be defined as a *reversible adiabatic disturbance* of the system, if it satisfies the following conditions:—

- (i.) The variation is effected infinitely slowly with respect to the motions of the system; more accurately: in a time so long that each coordinate has gone up and down many times between its limits, the a have changed by an amount infinitesimal of the 1st order.
- (ii.) Approximately the $\frac{da}{dt}$ are constants.
- (iii.) During the process the equations

$$\frac{dq_k}{dt} = \frac{\partial H}{\partial p_k}; \quad \frac{dp_k}{dt} = -\frac{\partial H}{\partial q_k} \quad . \quad . \quad . \quad (3)$$

remain valid †.

* In the problems studied by Epstein and others among the coordinates an azimuthal angle ϕ occurs, which can increase indefinitely. The configuration of the system is, however, periodic with respect to this variable. An increase of ϕ by 2π takes the place of the libration of the other coordinates. With some slight modifications the considerations given above are valid also for coordinates of this kind.

† This is for instance always the case, if only those a which occur in the function of forces are varied.

If we bring the system from a given state of motion, in which the a and the constants of integration of the equations of motion have definite values, in a reversible-adiabatic way to another state of motion, the values of the constants of integration will change. Let $c=f(q, p, a, t)$ be a first integral of the equations of motion, then, by means of condition (iii.), we can prove that the total change of c during the adiabatic process amounts to

$$\delta c = \int \frac{\partial f}{\partial a} \cdot \frac{da}{dt} \cdot dt = \overline{\frac{\partial f}{\partial a}} \cdot \delta a^* \quad . \quad . \quad . \quad (4)$$

(For the sake of simplicity we have supposed that only *one* of the a is varied.) The dash over $\frac{\partial f}{\partial a}$ denotes an appropriately determined *mean value*. According to condition (ii.) we may take the mean with respect to the time, while according to (i.) we may take the mean with respect to the time in the *undisturbed motion*.

An *adiabatic invariant* will now be defined as a function of the constants of integration and of the parameters, the total variation of which during the adiabatic process is *zero* †.

2.

Suppose that the equations of motion of the mechanical system are integrated. Then it is always possible to express the p as functions of the q , the a , and of n (canonical) constants of integration $\alpha' \dots \alpha^n$. The “conditionally periodical” systems are characterized by the following property: each momentum p_k can be expressed as a function which contains only q_k together with the a and α :

$$p_k = \sqrt{F_k(q_k, \alpha' \dots \alpha^n, a)} \ddagger \quad . \quad . \quad . \quad (5)$$

In connexion with supposition A (§ 1) the functions F_k must

* Cf. the paper in the Proc. Acad. Amsterdam.

† If an integral $c=f$ is independent of the a , c will be an adiabatic invariant, e.g. the moment of momentum in the motion under the influence of central forces.

‡ Geometrical interpretation of this formula: If we draw a q - p -diagram for the coordinate q_k , the point (q, p) describes a closed curve, the form of which is independent of the values of the other q 's.

satisfy the conditions that :

(a) every equation $F_k=0$ possesses (at least) two consecutive simple roots ξ_k, η_k , between which F_k is positive *;

(b) at a certain instant every coordinate lies between the corresponding roots.

Then it can be demonstrated that the motion of each q_k is a libration between these roots †.

In immediate connexion with the equations (5) we have the system of n first integrals :

$$\alpha^m = H^m(q, p, a) (6)$$

One of the α , for instance α' , is equal to the total energy of the system ; then H' is the Hamiltonian function.

If now we consider the "phase-integrals"

$$I_k = 2 \int_{\xi_k}^{\eta_k} p_k dq_k = 2 \int_{\xi_k}^{\eta_k} dq_k \sqrt{F_k} = I_k(\alpha' \dots \alpha^n, a) . . . (7)$$

it is found after some calculations. that the variation of I_k during an adiabatic disturbance of the system is

$$\delta I_k = \delta a \cdot \left[2 \int_{\xi_k}^{\eta_k} dq_k \frac{\partial \sqrt{F_k}}{\partial a} + \sum_m \frac{\partial H^m}{\partial a} \cdot 2 \int_{\xi_k}^{\eta_k} dq_k \frac{\partial \sqrt{F_k}}{\partial \alpha^m} \right]^\ddagger . . . (8)$$

In order to show that the quantities I_k are adiabatic invariants (in other words : that $\delta I_k = 0$), we need a method to

calculate the mean values $\frac{\partial H^m}{\partial a}$. This may be obtained by studying the properties of periodicity of the systems under consideration, as shown in the next section.

* The radical sign over F_k has been introduced in order that in the common cases the function F_k may be rational. Otherwise the condition (a) would have had the form: p_k has roots of the order 1/2 at the points $q_k = \xi_k, q_k = \eta_k$. The fact, that the motion of q_k is a libration, and the properties of periodicity of these systems (see § 3) are based upon the function $p_k(q_k)$ having branch-points at ξ_k and η_k .

† Cf. Charlier, l. c.

‡ At the limits of the integration the integrand $\sqrt{F_k}$ is equal to zero, so that we may omit the variations of these limits. In the case of an azimuthal angle ϕ the variation of the limits has no influence either, as it has the same value for $\phi = \phi_0$ and $\phi = \phi_0 + 2\pi$.

3.

Let us denote $\frac{\partial \sqrt{F_k}}{\partial \alpha^i}$ by f_{ki} ; the determinant of the n^2 functions f_{ki} may be F ; its minors, F^k ; and $f^{ki} = F^{ki}/F$.

We will introduce the quantities

$$t = \sum_k \int^{q_k} dq_k \cdot f_{ki} \quad . \quad . \quad . \quad . \quad . \quad (9)$$

During the motion of the system $t_2 \dots t_n$ are constants, whereas $t_1 = t - t_0$. All phases of our system may be characterized by the values of the q and p , or by those of the q and α , or by those of the t and α . We will study the representation upon each other of the following two n -dimensional spaces (obtained by putting the α equal to constants):—

- (i.) the q -space (bounded by the surfaces $q_k = \xi_k$; $q_k = \eta_k$);
- (ii.) the t -space.

The t are many-valued functions of the q with moduli of periodicity ω_{ki} *. Here

$$\omega_{ki} = 2 \int_{\xi_k}^{\eta_k} dq_k \cdot f_{ki} \quad . \quad . \quad . \quad . \quad . \quad (10)$$

is the increase of F_i , if q_k goes up and down once between ξ_k and η_k , while the other q remain constant †. Hence the t -space may be divided into “*period-cells*”: to congruent points of these cells the same point of the q -space corresponds. The representation of a period-cell in the q -space bounded according to (i.) is uniform; on the other hand, every point of the q -space is represented at more than one point of a period-cell, in such a way that the positive and negative values of $p_k = \sqrt{F_k}$ are separated.

We will put the determinant of the ω_{ki} equal to Ω ; its minors are Ω^{ki} ; and $\omega^{ki} = \frac{\Omega^{ki}}{\Omega}$. Ω is equal to the volume of a period-cell. In the t -space the motion of the mechanical system is represented by a straight line parallel to the axis of t_1 , which passes through the system of period-cells. If we replace each point of the line by its congruent point in one of the period-cells it may be demonstrated that in the general case the set of points obtained in this cell is every-

* Cf. Charlier, *l. c.*

† These integrals receive a simple meaning, if q_k is regarded as a complex variable. Cf. Sommerfeld, *Phys. Zeitschr.* xvii. (1916) p. 500.

where *dense* *. Now the mean of a quantity Z with respect to the time, *i. e.* the mean value of Z for all states represented by a great length of the t -line, may be replaced by the mean value of Z for all the points of one period-cell †. Hence

$$\bar{Z} = \frac{1}{\Omega} \int \dots \int dt_1 \dots dt_n \cdot Z \quad . \quad . \quad . \quad (11)$$

(the integration is effected over the volume of one period-cell).

Transforming from the t to the q as variables, the formula becomes

$$\bar{Z} = \frac{1}{\Omega} \int \dots \int dq_1 \dots dq_n \cdot F \cdot Z \quad . \quad . \quad (12)$$

as according to (9) $\frac{\partial t_i}{\partial q_k} = f_{ki}$.

If we use this formula to calculate the quantities $\frac{\partial H^m}{\partial a}$, after some transformations we find

$$\frac{\partial H^m}{\partial a} = - \sum_l \omega^{lm} \cdot 2 \int_{\xi_l}^{\eta_l} dq_l \frac{\partial \sqrt{F_l}}{\partial a} \dagger. \quad . \quad . \quad (13)$$

Introducing the values found in equation (13) into equation (8), we find that $\delta I_k = 0$. Thus it has been demonstrated that the “*phase-integrals*” I_k are invariants during an adiabatic disturbance of the system.

4. Summary.

For mechanical systems possessing the following properties:—

- (1) each momentum p_k can be expressed as a function of the corresponding coordinate q_k together with the constants of integration of the n first canonical integrals and with certain parameters;

* This theorem is due to Stäckel. It is founded upon theorems by Jacobi and Kronecker. See for instance Kronecker, *Werke*, iii. 1, p. 47.

A necessary condition is the following: between the quantities ω_j^1 (the so-called “mean motions”) there may not exist any relations of the form

$$\sum_j m_j \omega_j^1 = 0,$$

where the m_j are integral numbers.

† For a demonstration of this the reader may be referred to the paper in the Proc. Acad. Amst. The demonstration is founded upon a development of the function Z in a multiple Fourier-series.

‡ Cf. the paper in the Proc. Acad. Amst.

- (2) the motion of each coordinate is a libration ;
 (3) between the mean motions ω^{j1} there do not exist any relations of commensurability:
 has been demonstrated that the “*phase-integrals*”
 $I_k = \int p_k dq_k$ are adiabatic invariants for infinitely slow changes of the parameters, in the sense defined by Ehrenfest.

A separate treatment is necessary for those systems between the mean motions of which relations of commensurability exist of the form $\sum_j m_j^\mu \omega^{j1} = 0$. It may be shown* that if we limit ourselves to those adiabatic disturbances which do not violate these relations, at least some linear combinations of the phase-integrals (with integral coefficients) are invariants. These combinations have the form

$$Y_s = \sum r_s^k \cdot I_k,$$

where the coefficients $r_s^1 \dots r_s^n$ are a primitive set of *integral* roots of the equations

$$\sum_j m_j^\mu x^j = 0.$$

As has been shown by Schwarzschild and Epstein †, the total energy α' of the mechanical system when expressed in the I_k depends only on linear combinations of these of the above form.

Hence by “*quanticising*” (equating to an integral multiple of Planck’s h) the invariants I_k in the general case, or Y_s in the special cases last mentioned, it is always possible to obtain a set of determinate values for the total energy.

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Postscriptum.—In Proc. Acad. Amst. xxv. (1916) p. 1055, a more general treatment of adiabatic invariants is given, which is based upon the integration of the equations of motion by trigonometric series.

The following difficulty must yet be mentioned: during the adiabatic affection the mean motions ω^{j1} change, and hence their ratios pass through rational values. It has to be examined what influence this can have.

* Proc. Acad. Amst. xxv. (1916) p. 918.

† K. Schwarzschild, *l. c.*; P. Epstein, *Ann. d. Phys.* li. (1916) p. 180.

L. *Molecular Refractivity and Atomic Interaction. II.* By L. SILBERSTEIN, *Ph.D., Lecturer at the University of Rome* *.

IN what follows, my first paper on this subject, *Phil. Mag.* vol. xxxiii. pp. 92-128, will be shortly referred to as I., and, if not otherwise stated, all symbols will have their previous meaning.

1. *Atomic Interaction; Corrigendum.*

By an inadvertence formula (4), p. 100, I., has been written for "the whole force" on the i -th electron due to the j -th atom (or j -th doublet). That formula represents, obviously, that part of the force which is due to the axial component alone of the displacement \mathbf{r}_j . The mutual distance R of the two atomic centres being large as compared with r_j , the j -th atom acts as an ordinary, and well familiar, doublet, and exerts on the dispersive electron of the i -th atom *the total force*

$$\mathbf{F}_{ij} = \frac{e_i e_j}{4\pi R^3} [3\mathbf{u}(\mathbf{u}\mathbf{r}_j) - \mathbf{r}_j],$$

where \mathbf{u} is a unit vector drawn from the i -th to the j -th centre, or *vice versa* †, the charges e_i , e_j being now taken in rational units. In Cartesians, if ξ , η , ζ are the rectangular coordinates of j , with origin in i , and r_x , r_y , r_z the components of the displacement \mathbf{r}_j , the components of the bracketed vector will have the familiar form $r_x \left(\frac{3\xi^2}{R^2} - 1 \right) + 3r_y \frac{\xi\eta}{R^2} + 3r_z \frac{\xi\zeta}{R^2}$, etc.

Let us write $\mathbf{p} = e\mathbf{r}$ for the electric moment of any doublet. Then the above fundamental formula will become

$$\mathbf{F}_{ij} = \frac{e_i}{4\pi R^3} [3\mathbf{u}(\mathbf{u}\mathbf{p}_j) - \mathbf{p}_j]. \quad . \quad . \quad . \quad (1)$$

The axial component of this force is $\frac{e_i(\mathbf{p}_j \cdot \mathbf{u})}{2\pi R^3}$, as in I., while the transversal part is given, in size and direction, by the vector $e_i[\mathbf{u}(\mathbf{u}\mathbf{p}_j) - \mathbf{p}_j]/4\pi R^3$. The latter is, obviously, in general, of the same order as the axial component and can,

* Communicated by the Author.

† This is immaterial, since \mathbf{u} enters only through the dyad $\mathbf{u} \cdot \mathbf{u}$ which retains its value on changing the sign of \mathbf{u} .

therefore, by no means be neglected. Thus, all of our previous formulæ for axial oscillations, axial refractivity, etc., remain valid, while those associated with transversal oscillations have to be corrected in accordance with formula (1).

The resultant force \mathbf{F}_i on the i -th electron due to the remaining atoms of the molecule will be the sum of vectors of the type of (1),

$$\mathbf{F}_i = \sum \mathbf{F}_{ij}, \quad j \neq i.$$

Thus \mathbf{F}_i will be a linear vector function of $\mathbf{p}_2, \mathbf{p}_3, \dots, \mathbf{p}_\kappa$, the moments of the second, third, etc., and κ -th doublet of the molecule, and so on. Let, again, γ_i be the squared free frequency of the i -th electron, and let us denote by \mathbf{G} the force, per unit charge, due to the doublets contained in the neighbouring molecules and due to the external field \mathbf{E} (incident light). Then, for monochromatic light of squared frequency γ , and writing again $B_i = e_i^2/m_i$, the equation of motion of the i -th electron reduces to

$$(\gamma_i - \gamma)\mathbf{p}_i - \sum \frac{B_i}{4\pi R_{ij}^3} [3\mathbf{u}(\mathbf{u}\mathbf{p}_j) - \mathbf{p}_j] = B_i \mathbf{G} \quad (2)$$

There are κ of such equations ($i=1, 2, \dots, \kappa$) for each molecule. In the simplest case of a gas in normal conditions the perturbation due to foreign molecules is negligible, and then we have simply $\mathbf{G} = \mathbf{E}$. For other bodies the difference of these two vectors will be a complicated function of the data fixing the arrangement of the molecules, as will be seen later on in some concrete examples. The refractive properties of the body considered as an aggregate of such molecules will follow from (2) and from the usual relation

$$(K-1)\mathbf{E} = \mathfrak{N} \sum \overline{\mathbf{p}_i}, \quad (3)$$

where \mathfrak{N} is the number of molecules per unit volume, $K = \mu^2$, as before, and $\overline{\mathbf{p}_i}$ the average of \mathbf{p}_i taken over a "physically small" volume, as in the current electron theory of dispersion.

2. *Refractivity of Diatomic Gases.*

Taking up again the case of diatomic molecules, let us apply the suffixes $i=1, 2$ to all the attributes of the two atoms composing each molecule. Let the substance consisting of these molecules be a gas in normal conditions. Then

$\mathfrak{N} = 2.76 \cdot 10^{19} \text{cm.}^{-3}$, so that the average distance of neighbouring molecules is of the order of $L = 3.3 \cdot 10^{-7}$, while the critical distance R_c of the atomic centres within a molecule is of the order 10^{-8} , and in some cases even smaller than that. Thus the ratio R_c/L is a small fraction, like $1/40$ or $1/50$, and since all optical perturbations are brought about essentially through the variation of the free frequencies, the influence of neighbour molecules, being represented by $(R_c/L)^3 \doteq 10^{-5}$, will be practically evanescent. Under these circumstances we have simply

$$\mathbf{G} = \mathbf{E},$$

and the general system of equations (2) gives, for each molecule, the two equations

$$\left. \begin{aligned} (\gamma_1 - \gamma) \mathbf{p}_1 - \frac{B_1}{4\pi R^3} [3\mathbf{u}(\mathbf{u} \mathbf{p}_2) - \mathbf{p}_2] &= B_1 \mathbf{E}, \\ (\gamma_2 - \gamma) \mathbf{p}_2 - \frac{B_2}{4\pi R^3} [3\mathbf{u}(\mathbf{u} \mathbf{p}_1) - \mathbf{p}_1] &= B_2 \mathbf{E}. \end{aligned} \right\} \quad (4)$$

Here R is the mutual distance of the two atomic centres, and \mathbf{u} a unit vector coinciding in direction with the *molecular axis* 12 or 21.

Consider, first, the ideal case in which the axes of all molecules are parallel to one another. Let a_i be the axial, and t_i the transversal component of \mathbf{p}_i , and E_a , E_t the corresponding components of \mathbf{E} , the electric vector in the incident light. Then (4) will split into

$$(\gamma_1 - \gamma) a_1 - \frac{B_1 a_2}{2\pi R^3} = B_1 E_a; \quad (\gamma_2 - \gamma) a_2 - \frac{B_2 a_1}{2\pi R^3} = B_2 E_a, \quad (4a)$$

and

$$(\gamma_1 - \gamma) t_1 + \frac{B_1 t_2}{4\pi R^3} = B_1 E_t; \quad (\gamma_2 - \gamma) t_2 + \frac{B_2 t_1}{4\pi R^3} = B_2 E_t. \quad (4t)$$

At the same time we shall have $\bar{\mathbf{p}}_i = \mathbf{p}_i$, and therefore, by (3),

$$(K_a - 1) E_a = \mathfrak{N}(a_1 + a_2); \quad (K_t - 1) E_t = \mathfrak{N}(t_1 + t_2), \quad (3')$$

where $K_a = \mu_a^2$, $K_t = \mu_t^2$; μ_a , μ_t being the corresponding refractive indices.

Now, the axial equations (4a) are identical with those

given in I., and so are (3'). Thus we have for the *axial* molecular refractivity of the orientated aggregate,

$$N_a = \frac{1}{3}(\mu_a^2 - 1) \frac{M}{d}^*,$$

precisely as in I. (with $4\pi R^3$ instead of R^3),

$$N_a = \frac{N_1 + N_2 + 2sN_1N_2}{1 - s^2N_1N_2}, \quad s = \frac{\alpha}{2\pi R^3}, \quad \dots \quad (5a)$$

where $N_i = \frac{B_i}{\alpha(\gamma_i - \gamma)}$ are the atomic refractivities of the constituents and $\alpha = 3m_H/1.008 = 4.88 \cdot 10^{-24}$ gr. The correct transversal equations (4t), however, differ from the original ones (in which the terms $B_i t_j / 4\pi R^3$ have been absent). Thus the *transversal* molecular refractivity $N_t = \frac{1}{3}(\mu_t^2 - 1) \frac{M}{d}$ will be different from that given in I. Its correct value, however, can be derived without much additional trouble. In fact, the left hand members of (4t) differ from those of (4a) only so far as $-2\pi R^3$ is replaced by $+4\pi R^3$. In order, therefore, to obtain N_t from N_a we have only to write, in (5a), $-\frac{1}{2}s$ instead of s . Consequently, the transversal molecular refractivity will be

$$N_t = \frac{N_1 + N_2 - sN_1N_2}{1 - \frac{1}{4}s^2N_1N_2}. \quad \dots \quad (5t)$$

Thus, *neither the axial nor the transversal refractivity of the compound obeys the additive law*. The real departure from additivity is, therefore, even more radical than has been asserted in the first paper, p. 104. At the same time *all the free frequencies* belonging to the molecule, those corresponding to axial as well as to transversal oscillations, differ from the atomic ones. The new axial frequencies are as in I, and the transversal ones will be given presently.

Isotropic Gas.—Let now the directions of the molecular axes be haphazardly distributed, as is the case in a real

* The irrelevant constant factor $\frac{1}{3}$, a degeneration of $(\mu_a^2 + 2)^{-1}$, is inserted only to make the expression uniform with the "molecular refractivity" as usually defined; M stands for the molecular weight and d for the density of the substance, as before.

gas. Then the molecular refractivity of the diatomic gas,

$$N = \frac{1}{3}(\mu^2 - 1) \frac{M}{d} \doteq \frac{2}{3}(\mu - 1) \frac{M}{d}, \text{ will be}$$

$$N = \frac{1}{3}N_a + \frac{2}{3}N_t,$$

that is, by (5a) and (5t), and writing Σ for the *sum*, and Π for the *product* of the two atomic refractivities N_1, N_2 ,

$$N = \frac{1}{3} \frac{\Sigma + 2s\Pi}{1 - s^2\Pi} + \frac{2}{3} \frac{\Sigma - s\Pi}{1 - \frac{1}{4}s^2\Pi} \cdot \cdot \cdot \cdot (5)$$

This is the required formula, valid for any diatomic gas.

The *free frequencies* belonging to the molecule will be obtained by equalling to zero the determinant of the equations (4a) and that of (4t). The former gives for the squared free frequencies γ_a , corresponding to axial oscillations, as in I.,

$$\gamma_a', \gamma_a'' = \frac{1}{2}(\gamma_1 + \gamma_2) \mp \frac{1}{2} \left[(\gamma_1 - \gamma_2)^2 + \frac{4B_1B_2}{\alpha^2} s^2 \right]^{1/2}, \quad (6a)$$

and the latter gives for γ_t , corresponding to transversal oscillations, on simply replacing s by $-\frac{1}{2}s$,

$$\gamma_t', \gamma_t'' = \frac{1}{2}(\gamma_1 + \gamma_2) \mp \frac{1}{2} \left[(\gamma_1 - \gamma_2)^2 + \frac{B_1B_2}{\alpha^2} s^2 \right]^{1/2}. \quad (6t)$$

Thus, *none of the original frequencies, and therefore, of the atomic bands, will remain in the absorption spectrum of the compound.* The dispersion curve will be entirely modified by atomic interaction, to an extent depending on the value of $\sqrt{B_1B_2}/R^3$. Yet, the sum of the squared new frequencies will be equal to that of the original or atomic ones. In fact, as has already been remarked in I., $\gamma_a' + \gamma_a'' = \gamma_1 + \gamma_2$; and so also, by (6t), $\gamma_t' + \gamma_t'' = \gamma_1 + \gamma_2$. Remembering that each of the γ_t counts for two (inasmuch as it belongs to two mutually perpendicular transversal oscillations), and denoting the new frequencies summarily by γ' , we can express the said *conservation of the sum of squared frequencies* by writing

$$\Sigma \gamma' = \Sigma \gamma_i = 3(\gamma_1 + \gamma_2) \cdot \cdot \cdot \cdot (7)$$

This *invariance* with respect to mutual action is a general property, valid for *any* number of interacting atoms. The proof is easily obtained by examining the determinant of the corresponding system of linear equations.

Subcase: Equal Atoms.—If the molecule consists of two equal atoms, that is if the gas is of the type of H_2 , we have $N_1 = N_2 = N_0$, say, and $\gamma_1 = \gamma_2 = \gamma_0$, $B_1 = B_2 = B$. The molecular refractivity of such a gas is, by (5),

$$N = 2N_0 \frac{1 - \frac{1}{2}sN_0}{(1 - sN_0)(1 + \frac{1}{2}sN_0)}, \quad . \quad . \quad . \quad (8)$$

where $s = \alpha/2\pi R^3$, as above. Applications of this formula * to ordinary hydrogen, oxygen, and nitrogen gas will be given presently.

The free frequencies (6a), (6t) are given, in the present case, by

$$\gamma_a', \gamma_a'' = \gamma_0 \mp \frac{Bs}{\alpha}; \quad \gamma_t', \gamma_t'' = \gamma_0 \mp \frac{1}{2} \frac{Bs}{\alpha} \quad . \quad . \quad . \quad (9)$$

The absorption spectrum will thus consist of *four* lines or bands, all different from the atomic one (γ_0). Two of these bands, γ_t'' , γ_a'' , will be *ultra*- γ_0 , and two, γ_t' , γ_a' , will be *infra*- γ_0 . In ascending order of wave-lengths we shall have

$$\lambda_a'', \lambda_t'', (\lambda_0), \lambda_t', \lambda_a',$$

λ_0 being abolished by interaction. The greatest of these wave-lengths being λ_a' , corresponding to $\gamma_a' = \gamma_0 - Bs/\alpha$, the critical distance R_c , determining the limit of optical stability (cf. I.) will be given by

$$s_c \equiv \frac{\alpha}{2\pi R_c^3} = \frac{\alpha\gamma_0}{B}, \quad . \quad . \quad . \quad (10)$$

and the condition of stability will be $s < s_c$.

Returning to (8), let us remember that $N_0 = B/\alpha(\gamma_0 - \gamma)$, $B = e^2/m$. If λ is the wave-length and $u = 1/\lambda^2$, then $\gamma = 4\pi^2 c^2 u$. Writing, therefore,

$$b_0 = \frac{e^2/c^2}{4\pi^2 m \alpha} \frac{1}{u_0}, \quad g_0 = \frac{b_0}{u_0}, \quad \frac{b_0^2}{g_0} = k_0, \quad . \quad . \quad . \quad (11)$$

as in Phil. Mag. Feb. 1917, we shall have

$$N_0 = \frac{k_0}{u_0 - u} \doteq b_0 + g_0 u, \quad . \quad . \quad . \quad . \quad (12)$$

since u_0 falls into the extreme ultra-violet and since in the concrete examples to be treated below u will be limited to the visible region of the spectrum. By (11), and writing

* Which replaces the erroneous formula (2) of the Note published in Phil. Mag. for February, 1917, p. 215. The numerical results given in that Note will be recalculated, a little further on, by means of the present formula (8).

$e' = e / \sqrt{4\pi}$ for the charge in ordinary (irrational) electrostatic units,

$$k_0 = \frac{1.008}{3\pi} \frac{e'/c}{m} \frac{e'/c}{m_H} \dots \dots \dots (11a)$$

Substituting (12) in (8), developing and rejecting the second and the higher powers of $g_0 u$, we have, for the molecular refractivity of the diatomic gas,

$$N = b + gu, \dots \dots \dots (13)$$

$$\left. \begin{aligned} \text{where } b &= 2b_0 \frac{1 - \frac{1}{2}b_0 s}{(1 - b_0 s)(1 + \frac{1}{2}b_0 s)}, \\ g &= b \frac{1 - b_0 s + \frac{3}{4}b_0^2 s^2}{u_0(1 - b_0 s)(1 - \frac{1}{4}b_0^2 s^2)} \end{aligned} \right\} \dots \dots \dots (14)$$

These are the *refraction-* and the *dispersion coefficient* of the gas in terms of the atomic coefficients b_0 , g_0 and the inter-atomic distance involved in s . Writing, analogously to k_0 ,

$$k = b^2/g,$$

we have, from (14),

$$k = 2k_0 \frac{(1 - \frac{1}{2}b_0 s)^2}{1 - b_0 s + \frac{3}{4}b_0^2 s^2},$$

whence

$$sb_0 = \frac{2k_0 - k \pm 2\sqrt{k(k_0 - \frac{1}{2}k)}}{k_0 - \frac{3}{2}k} \dots \dots \dots (15)$$

This is the correct formula to be employed instead of formula (12) in a previous Note (Phil. Mag., Feb. 1917, p. 218). As in that Note, let ϵ be the value of the right-hand member of (11a) which would correspond to an electron proper, *i. e.*

$$\epsilon = 0.107 \cdot 1.77 \cdot 10^7 \cdot 9650 = 1.83 \cdot 10^{10} \frac{\text{cm.}}{\text{gr.}}, \dots (16)$$

and let us assume again that any atomic k_0 is an *exact multiple of the electronic value*,

$$k_0 = n\epsilon, \dots \dots \dots (17)$$

n being the *smallest integer* compatible with the conditions of the problem. Now, notwithstanding the above correction of the transversal part of the interaction, the expression under the radical in (15) has remained exactly as before. Thus, k being essentially positive and sb_0 real, n will again be the smallest integer satisfying the inequality

$$k_0 = n\epsilon > \frac{1}{2}k. \dots \dots \dots (18)$$

The condition of stability, is by (10), in terms of b_0 ,

$$sb_0 < 1, \dots \dots \dots (19)$$

the critical distance R_c being given by $\frac{1}{s_c} = \frac{2\pi R_c^3}{a} = b_0$.

The coefficients b , g , and therefore k , being known from the observed refractivity of the diatomic gas, and k_0 being determined by (18), the product sb_0 will be found by means of (15). And inserting sb_0 in (14) we shall obtain the atomic coefficients b_0 , g_0 , and at the same time the value of s and therefore also the interatomic distance R .

3. Hydrogen, Oxygen, and Nitrogen.

The coefficients for these diatomic gases, as given by their observed refractivities, at least within the visible region of the spectrum, are (Phil. Mag. Feb. 1917, pp. 219-221),

$$b = 2.044_5; \quad g = 1.27_9 \cdot 10^{-10}; \quad k = \frac{b^2}{g} = 3.268 \cdot 10^{10}, \quad (\text{H}_2)$$

$$b = 3.967; \quad g = 2.50 \cdot 10^{-10}; \quad k = 6.295 \cdot 10^{10}, \quad (\text{O}_2)$$

$$b = 4.409; \quad g = 1.91 \cdot 10^{-10}; \quad k = 10.18 \cdot 10^{10}. \quad (\text{N}_2)$$

Thus, by (16) and (18), the values of k_0 to be attributed to the atoms of hydrogen, oxygen, and nitrogen are

$$k_0 = \epsilon, \quad 2\epsilon, \quad 3\epsilon,$$

respectively. Substituting these numbers and the above numerical values of k into (15), I find, for hydrogen, oxygen, and nitrogen, respectively,

$$sb_0 = 0.3932, \quad 0.4436, \quad 0.2962,$$

each satisfying abundantly the condition of stability, (19). Substituting these values of sb_0 , and the above b 's, in (14), we find the required atomic coefficients b_0 , $u_0 = \lambda_0^{-2}$, whence also s and therefore R . The atomic attributes thus obtained for the three elements are collected in Table I., which, besides the coefficients k_0 and the free wave-lengths λ_0 , contains also the critical distances R_c of two equal atomic centres, determined by $2\pi R_c^3 = \alpha b_0$.

TABLE I.

| Atom. | $\lambda_0 \cdot 10^8$. | k_0 . | Atomic Refractivity N_0 . | | | Diatomic Molecule. | |
|-------|--------------------------|-----------------------------------|-----------------------------|-----------|------------|--------------------|--------------------|
| | | | H_α | H_β | H_γ | $R \cdot 10^8$. | $R_c \cdot 10^8$. |
| H ... | 710.8 | $\epsilon = 1.83 \cdot 10^{10}$. | 0.936 | 0.945 | 0.950 | 1.222 | 0.895 |
| O ... | 688.0 | 2ϵ | 1.752 | 1.768 | 1.777 | 1.448 | 1.104 |
| N ... | 617.2 | 3ϵ | 2.110 | 2.125 | 2.134 | 1.764 | 1.175 |

The reader will notice that the *interatomic distances* R in the actual molecules of the gases H_2 , O_2 , N_2 are considerably larger than the corresponding critical values (R_c), thus satisfying the condition of optical stability. For the sake of future reference in working out numerical examples, the values of the *atomic refractivities*, calculated by means of the formula

$$N_0 = \frac{k_0}{u_0 - u}, \quad u = \lambda^{-2} \quad . \quad . \quad . \quad (12)$$

for the first three members of the Balmer series, are given under the usual headings H_α , H_β , H_γ . There is nothing surprising in the fact that our atomic refractivities differ considerably from those hitherto used by chemists (*cf.* I., p. 94).

Comparison with Results of Kinetic Theory of Gases.—It may be interesting to compare the above interatomic distances, viz., in H_2 , O_2 , N_2 respectively,

$$R = 1.222 \quad 1.448 \quad 1.764.10^{-8}, \quad . \quad . \quad (20)$$

with the semidiameters $\frac{1}{2}\sigma$ of the corresponding molecules, obtained by various methods based on the kinetic theory of gases. Let us take for this purpose Jeans' latest *free-path* semidiameters*,

$$\frac{1}{2}\sigma = 1.34 \quad 1.81 \quad 1.90.18^{-8}, \quad . \quad . \quad (J.)$$

which seem thoroughly well-founded, the more so as they represent, at the same time, the viscosity-, the heat conduction- and the diffusion-values, *i. e.* all values following from the free-path phenomena. They differ only, *as they should*, from the Boyle's-Law values of the semidiameters of the corresponding molecules. To avoid confusion, these latter will be denoted by $\frac{1}{2}\sigma_B$, and the former, free-path ones, simply by σ .

The above kinetic semidiameters (J.) are considerably greater than our interatomic distances R . The two sets, however, show a marked *parallelism*, and not only a mere agreement in order of magnitude. A geometric interpretation of this parallelism may be of some interest.

* J. H. Jeans, *Dyn. Theory of Gases*, 2nd edition (1916), p. 341, where $\pi = 2.75.10^{19}$, agreeing with the value I have adopted throughout, is taken for Loschmidt's number. In the 1st edition of his work (1904) Jeans has adopted the considerably higher value 4.10^{19} . This I have noticed only through the huge contrast afforded by the figures of Jeans' 2nd edition (which is only in a small extent due to the replacing of the original coefficient 0.44 by Chapman's 0.499). The number 2.75 or $2.76.10^{19}$ has been in fairly general use since 1901.

At first sight it would seem that, if each atom is a sphere of radius r , we should have $\frac{1}{2}\sigma = \frac{1}{2}R + r$ (and in the case of contact, for example, $\frac{1}{2}\sigma = R$), assuming, of course, that our optical centres 1, 2 are the centres of the atomic spheres. This relation between R and σ , r would hold, in fact, if the system had a sufficiently rapid motion round the mass-centre O with chaotically changing axes of rotation; for then the molecule would behave, for purposes of encounter, as a full sphere of radius $\frac{1}{2}\sigma = \frac{1}{2}R + r$. But, contrary to the opinion of some physicists, this is by no means the case. If there is any rotation, it is certainly not rapid enough for the rushing neighbour molecules. The radius $\frac{1}{2}\sigma$ of the equivalent sphere is not $\frac{1}{2}R + r$ but rather (much the same as if the molecule was not rotating at all) equal to the average $\bar{\rho}$ of the semidiameters ρ drawn from the centre O of the system to its "surface" (more rigorously, the semidiameter corresponding to the mean area of section of tangential cylinders). We shall not be far from truth if we substitute for the two spheres* an ellipsoid of revolution, of semiaxes

$$a = \frac{1}{2}R + r, \quad b = r. \quad . \quad . \quad . \quad . \quad (21)$$

The deeper the interpenetration of the atomic spheres the more justified this substitution, but it would be sufficiently accurate even in the case of contact. The corresponding mean $\bar{\rho} = \frac{1}{2}\sigma$ is easily found to be

$$\bar{\rho} = \frac{2b}{\pi} F_{\theta}, \quad \cos \theta = \frac{b}{a}, \quad . \quad . \quad . \quad . \quad (22a)$$

where F_{θ} is the complete elliptic integral of the first species whose modulus is $\sin \theta$. Thus, with the semiaxes (21), and writing for the moment

$$x = 2r/R,$$

we shall have, for the ratio of the (free-path) semidiameter of the molecule to the interatomic distance R ,

$$\frac{\sigma}{2R} = \frac{x}{\pi} F_{\theta}; \quad \cos \theta = \frac{x}{1+x}. \quad . \quad . \quad . \quad (22)$$

If, for instance, the spheres are in contact ($x=1$), we have $\theta=60^{\circ}$, and $\frac{1}{2}\sigma : R = 0.6864$. This ratio increases with increasing depth of interpenetration of the atomic spheres. In general, σ and R being known, from the kinetic theory and from the present dispersion theory, we have in (22) a transcendental equation for x , and therefore for the atomic

* The spherical form is assumed for the sake of simplicity only, and can later be given up for a more general one. In fact, the circumstance that σ_B (Boyle-diameter) differs from σ (free-path) even for *monatomic* gases would suffice by itself to show that at least some of the single atoms themselves are not spherical, or, that the equivalent force-centres are not isotropic.

radius r . The equation is of a rather complicated kind. It is, however, conveniently solved by the process of successive approximations which leads very rapidly to a more than sufficiently correct result. In this manner*, and substituting for σ the values (J.) and for R the values (20), I find from (22), for the atomic radii of hydrogen, oxygen, and nitrogen, respectively,

$$r_{\text{H}} = 1.085, \quad r_{\text{O}} = 1.501, \quad r_{\text{N}} = 1.534 \cdot 10^{-8}. \quad (23)$$

These radii of the atomic spheres are based upon R and the free-path diameters equalled, approximately, to $2\bar{\rho}$.

Let us still consider the *Boyle-diameters* of the molecules. These diameters enter through the volume of the molecules and will thus be given by $\frac{4\pi}{3} \left(\frac{\sigma_{\text{B}}}{2}\right)^3 = \text{volume of the two atomic spheres minus that of the lenticular region of overlapping.}$ The latter could be easily calculated. Having, however, once replaced the diatomic molecule by the ellipsoid of revolution (21), let us keep to this substitute. Thus we shall have

$$\frac{1}{2}\sigma_{\text{B}} = (ab^3)^{1/3} = (r + \frac{1}{2}R)^{1/3}r^{2/3}. \quad (24)$$

By means of this formula, and using the interatomic distances R , we can predict what the Boyle-radii of the molecules should be. Let us take for this purpose the set (23) of atomic radii r which we have obtained a moment ago. Then, with R substituted from (20), formula (24) gives

$$\frac{1}{2}\sigma_{\text{B}} = \begin{matrix} \text{H}_2 & \text{O}_2 & \text{N}_2 \\ 1.260 & 1.711 & 1.785 \cdot 10^{-8}, \end{matrix} \quad (25)$$

while the values actually deduced from the deviation from Boyle's law are (Jeans, p. 342, not containing O_2):

$$\frac{1}{2}\sigma_{\text{B}} = 1.26 \quad \text{---} \quad 1.77 \cdot 10^{-8} \quad (J.)$$

The agreement is surprisingly good. Thus the free-path values σ appear connected with the Boyle-values σ_{B} through the dispersion theory.

In view of this result we shall adopt, for the *kinetic radii of the atoms* of hydrogen, oxygen, and nitrogen our above set (23), retaining ultimately but two decimal figures, *i. e.*

$$r_{\text{H}} = 1.09, \quad r_{\text{O}} = 1.50, \quad r_{\text{N}} = 1.53 \cdot 10^{-8}. \quad (23a)$$

The reader will have noticed that the interaction-theory of dispersion is *entirely independent* of these radii, and, in fact, of any concepts of size or shape of the molecules and of their component atoms. For in this theory the atom plays only, thus far, the part of an (optical) centre or point,

* Using a five figure table of $\log F_{\theta}$.

which is converted by external agents into an electric doublet, and the molecule is a system of such points. We shall, now and then, need the above radii *only* in order to estimate the kinetic dimensions of molecules composed of these three and of other atoms, or sometimes, to guide our choice among all the possible configurations of the atomic centres.

4. *Nitric Oxide, NO.*

The observed refractivity of this gas is, in normal conditions, for $\lambda = 0.589$ (Landolt-Börnstein's tables, 1912, p. 1019),

$$\mu - 1 = 2.94 \cdot 10^{-4} \text{ (Cuthbertson and Metcalfe).}$$

Observations for other wave-lengths are not quoted. Taking this value, we have for the molecular refractivity of nitric oxide, $N = \frac{2}{3} \frac{M}{d} (\mu - 1)$, with $M = 30.01$, $d = 1.342 \cdot 10^{-3}$,

$$N = 4.382, \text{ for } \lambda_D.$$

On the other hand, the atomic refractivities of nitrogen and of oxygen for the same wave-length are, by Table I. and by formula (12),

$$N_D = 2.114, \quad O_D = 1.757,$$

whence, their sum and their product,

$$\Sigma = 3.871, \quad \Pi = 3.714.$$

Substituting these values and the observed $N = 4.382$ into our general formula (5) for the molecular refractivity of a diatomic gas, we have the quartic equation for $s = \alpha/2\pi R^3$:

$$a_4 s^4 - a_3 s^3 - a_2 s^2 + a_0 = 0, \quad . \quad . \quad . \quad . \quad (26)$$

where

$$a_4 = N\Pi^2 = 60.430, \quad a_3 = 2\Pi^2 = 27.581,$$

$$a_2 = \Pi(5N - 3\Sigma) = 38.238, \quad a_0 = 4(N - \Sigma) = 2.044.$$

The only positive root of (26), satisfying the condition of stability, is, to four decimals*,

$$s = 0.2221.$$

This gives, for the interatomic distance in NO,

$$R = 1.518 \cdot 10^{-8} \quad . \quad . \quad . \quad . \quad (27)$$

By (23) the atomic radii r_O and r_N are but slightly different from one another. Thus we can, with sufficient accuracy, take for both atomic spheres the mean

$$r = \frac{1}{2}(r_O + r_N) = 1.517_5 \cdot 10^{-8},$$

* Of the remaining three roots of the quartic equation two are negative, viz. $s = -0.2822$ and -0.5201 , and are thus out of question, and one is positive, $s = 1.037$, but much too large to satisfy the condition of optical stability of the NO molecule.

and substitute for the two spheres the ellipsoid

$$a = \frac{1}{2}R + r = 2.277, \quad b = r = 1.518 \cdot 10^{-8}.$$

This gives for the semidiameter of the molecule NO, by (22 a),

$$\bar{\rho} = \frac{1}{2}\sigma = \frac{3.036 \cdot 10^{-8}}{\pi} F_{\theta}, \cos \theta = \frac{1.518}{2.277},$$

that is,

$$\frac{1}{2}\sigma = 1.840 \cdot 10^{-8}. \quad . \quad . \quad . \quad . \quad (28)$$

The free-path semidiameter of this molecule is, according to Jeans (*loc. cit.*, p. 341),

$$\frac{1}{2}\sigma = 1.86 \cdot 10^{-8} \quad . \quad . \quad . \quad . \quad . \quad (J.)$$

The coincidence is almost perfect. It thus serves also as an additional corroboration of the correctness of our atomic refractivities of nitrogen and oxygen and of our estimate of their atomic radii.

Substituting the above value of s into (5), the molecular refractivity of nitric oxide can be calculated for any λ , within the prescribed region at least. Since, however, the only observed refractivity is that for sodium light, the calculation can be omitted for the present.

The purpose of this Section has been chiefly to illustrate the application of the general formula (5) for diatomic gases. In order to be able to treat further, and more vital, concrete examples we shall have first to enlarge our meagre list of atomic refractivities, preferably by adding to the above three (H, O, N) that of carbon which we shall attempt to derive, with such rigour as is possible, from the optical properties of diamond. But before doing so it will be necessary to leave the gases and to investigate the rôle of interaction in more dense aggregates of molecules, viz. in solid crystals. The treatment, to be given in the next paper, of the simplest cubic and quasi-cubic arrangements of atomic centres will pave the way for some concrete and more complicated problems.

London, April, 1917,
Research Dept., Adam Hilger, Ltd.

LI. Notices respecting New Books.

Science Progress. No. 43. January 1917.

London: John Murray. Price 5s. net.

THIS number contains several articles and reviews of interest to the physicist. Dr. R. A. Houstoun gives a popular account of his new theory of colour vision first put forward in the Proceedings of the Royal Society for 1916. The popular account is hardly so convincing as the Royal Society paper; but this is no

doubt owing to the difficulties attending an attempt to express a mathematical problem in non-mathematical language. The new theory does away with the need of three distinct colour sensations (for which there is no histological evidence); and it bears considerable resemblance to the views which have been advocated by Edridge-Green for many years past. The fact that the phenomena of colour mixture can be described so satisfactorily in terms of the three-colour theory is apt to make one ignore the lack of microscopical evidence for it; moreover physicists are usually so little acquainted with the subjective phenomena of colour vision that the difficulty of explaining these by the same theory does not oppress them. This article and the original article are well worth careful study.

The number also contains an appreciatory note by D.O.W. on the recipients of the Nobel Physics Prizes for 1915, Professor W. H. Bragg and his son (with portraits). Also an illuminative essay by Dr. H. Bateman on the theory of integral equations and the calculus of operations and functions.

LII. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 456.]

February 7th, 1917.—Dr. Alfred Harker, F.R.S., President, in the Chair.

THE following communications were read:—

1. 'The Trias of New Zealand.' By Charles Taylor Trechmann, M.Sc., F.G.S.
2. 'The Triassic Crinoids from New Zealand collected by Mr. C. T. Trechmann.' By Francis Arthur Bather, M.A., D.Sc., F.R.S., F.G.S.
3. 'On a Spilitic Facies of Lower Carboniferous Lava-Flows in Derbyshire.' By Henry Crunden Sargent, F.G.S.

The igneous rocks of Derbyshire form a basic series, consisting mainly of lavas and sills, hitherto classed as olivine-dolerites and basalts, often associated with tuffs and agglomerates. All these rocks occur in Lower Carboniferous strata. The lavas were submarine and contemporaneous.

Specimens of the lavas from certain localities exhibit a trachytic structure, and possess affinities with both spilites and mugearites. These specimens are all intensely decomposed, feldspar being generally the only original mineral that is determinable. The alkali-content sometimes exceeds 7 per cent., potash being always important and sometimes predominant. The feldspar species are oligoclase and orthoclase, with generally a more basic plagioclase subordinate. Replacement by alkali-feldspar frequently occurs.

Field-evidence shows that these spilitic rocks, as a rule, underlie the basalts. A gradation may be traced between the two extremes of the series.

It is suggested that the whole series has been derived from

a common magma of normal basaltic type, and that, by the upward passage of gases through the magma, a relative concentration of the alkalis took place in its upper part, which was the earliest erupted. It is further suggested that the intense decomposition of the spilites is a case of auto-metamorphism, due to retention of volatile constituents resulting from the physical environment of a submarine flow.

An analogue to the radiolarian cherts and jaspers, generally associated with spilites in other localities, is found in Derbyshire in the quartz-rock and other siliceous rocks that frequently occur in proximity to volcanic vents.

Since the spilites appear to be differentiated from a normal basaltic magma, resulting largely from their physical environment, it is concluded that they do not form a separate suite of igneous rocks distinct from other alkaline rocks.

LIII. *Intelligence and Miscellaneous Articles.*

ARNOLD LOCKHART FLETCHER.

ON April the 30th Arnold Lockhart Fletcher died at Rouen of severe wounds received in action. He was in the 28th year of his age. During his short life he accomplished work of permanent value.

Arnold Fletcher was educated in various schools in England and Ireland, and entered Trinity College, Dublin, in 1906. He graduated in Arts and in Civil Engineering, obtaining the latter degree in 1909. Shortly after passing his finals in Engineering he was appointed Assistant in the Department of Geology—a subject in which he had displayed a keen interest as a student. During his tenure of this post the work of research in this Department was mainly confined to the distribution of radioactive elements. Most of Fletcher's papers are devoted to this subject. Various important materials were examined by him, using, at first, the method introduced by Strutt, and, later, the method by fusion. When a convenient means of estimating thorium emanation was devised, the search for this element was added to that of radium emanation.

Fletcher's papers on the radioactivity of rocks and minerals show him to be an enthusiastic worker who spared no pains to obtain reliable results. His paper on the radium content of Secondary Rocks well illustrates his minute care in research (*Phil. Mag.* Feb. 1912). This paper will, in the present writer's opinion, long remain the best work which has been done on these materials. Indeed it cannot be superseded, for it is a record of natural quantities which enter as essential data into geological science, and must retain its value unless some at present unknown source of error can be shown to exist.

This and several of his other papers show Arnold Fletcher as possessed of the most valued quality of the investigator—the determination to arrive at accuracy. But they also show him to be possessed of the inventiveness which continually improves upon

apparatus. His manipulative skill was remarkable, and he seemed specially at home in that sort of quick manipulation which involves keeping one's head while making adroit and quick movements.

He investigated the rocks of the Transandine Tunnel; of the Leinster Granite; of Antarctic regions and Secondary Rocks in general. He shared in the work of Halo measurement. Later (at this time working for a short period in the Royal College of Science for Ireland) he published an account of a method of determining the radium content of small quantities of radioactive minerals. All these papers appeared in the *Philosophical Magazine*. A paper on Sublimates appeared in the *Proceedings of the Royal Dublin Society*.

In November 1913 he became a Junior Inspector under the Department of Agriculture and Technical Instruction.

He was gazetted Second Lieutenant to the 4th Batt. of the Leinster Regiment in April 1915, and was attached to the Machine Gun Corps later on in recognition of work on machine gunnery. He held the rank of Lieutenant at the time of his death. He had been in France since Dec. 1916.

What honour is too great to pay to these young scientific men? They give up something more than life: a future of high ideals and aims.

J. J.

ON THE "WOLF-NOTE" IN BOWED STRINGED INSTRUMENTS.

I HAVE read with much interest Prof. Raman's paper under this head in No. 190 of this Journal, but I cannot agree with what is mentioned there on the cause of the mute-effect. Prof. Raman tells us that the frequency of maximum resonance of the bridge and associated parts of the belly gets altered by loading the bridge, and that "the explanation of the effect of a mute on the tone of the instrument is chiefly to be sought for in the effect of the loads applied on the frequencies of the principal free modes of vibration of the bridge and associated parts of the belly."

I suppose that the change of pitch of the note of maximum resonance of bridge, belly, &c. will practically be the same whether the bridge be loaded at its highest part or as low as possible and near to its left foot. Yet the difference of tone-quality is very large, as the experiments of M. de Haas and the writer of these lines have shown*: in the first case the sound is strongly damped—the ordinary mute-effect—, whereas in the second case only a very slight damping of the G-string is noticeable.

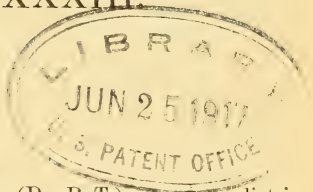
Secondly, I think the fall of pitch of the resonance note, caused by a mute, might perhaps explain an alteration of timbre for those notes whose pitch approaches that of the (lowered) resonance note, but I fail to see how it should explain the great change of tone-quality of even the highest notes on the E-string.

J. W. GILTAY.

Delft, Holland, 24th March, 1917.

* Proc. Roy. Soc. Amsterdam, January 1910.

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